INTRODUCTION TO GENERAL CHEMISTRY

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BY

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EXPERIMENTS IN INORGANIC CHEMISTRY

. . . je me suis imposé la loi de ne procéder jamais que
du connu à l'inconnu, de ne déduire aucune conséquence
qui ne dérive immédiatement des expériences et des ob-
servations, et d'enchaîner les faits et les vérités chimique
dans l'ordre le plus propre à en faciliter l'intelligence
aux commençants.

— Lavoisier's *Traité Élémentaire de Chimie.*
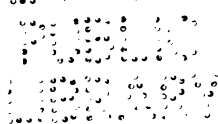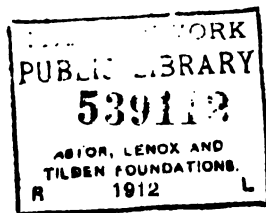
PREFACE

THIS book contains the material for a first year's course in chemistry. It is designed as an introduction to advanced study, providing a foundation which shall be broad and thorough. At the same time, as most students do not take more than a single year of the subject, I have endeavored to present it in such a way as to give them a fair idea of the nature of chemical study, of the methods by which our chemical knowledge has been gained, and of the relations which chemistry bears to everyday experiences and to industrial activities. Above all, I have tried to help the student to enter into the spirit of chemistry, and to acquire the scientific point of view. This is the most important service which a course in chemistry can render, and far outweighs the value of the facts which are learned.

The many textbooks on introductory chemistry which have appeared in the last few years are evidence of the differences of opinion as to the best mode of presenting the subject. This book is one more attempt to solve the problem. I am well aware of imperfections in the scheme, but trust it is a step in the right direction. My aim is to develop the subject in a natural manner, introducing new facts and ideas gradually, and discussing their relations and the theoretical explanations at points where such discussions will be welcomed by the student as summing up and interpreting what

has gone before. So far as possible, the progress is
from the familiar to the unfamiliar, from the known to
the unknown.

The manner of chemical inquiry by experiment and
of reasoning from the experimental results is made an
important part of the study. The quantitative relations
of chemistry have been emphasized, and the methods of
translating the results of weighing and measuring into
formulas have received many illustrations. Frequent
references are made to quantitative experiments de-
scribed in a little book recently published. These
experiments are all of the simplest character and, while
the results which they give are, of course, only approxi-
mations to those obtained in more exact work, they are
useful in aiding the student to understand the general
nature of the determinations which are the foundation
of the science, and to appreciate, at the same time,
the many precautions which are necessary for reliable
results. It is not intended that all of the experiments
referred to shall be performed, but many of them may
be made to advantage by the student or as demonstra-
tions by the instructor, while others are used for dis-
cussions and calculations.

I have made the synthesis of sulphuric acid and the
study of its composition the basis for the preparation
and study of the other acids and substances related to
them,—thus placing sulphuric acid, in the development
of the subject, in the position which it occupies in
actual practice. In the treatment of the different
elements and their compounds, a similar consideration
has led to some variety in the order of discussion; in
general, that substance — element or compound —

which is most familiar or from which the others are derived, is first described, and the other related substances then follow somewhat in the order of their importance.

As the book is to be used in connection with lectures or recitation talks and discussions, the text is succinct and, I trust, suggestive, leaving ample scope for enlargement and illustration. Pictures of apparatus and experiments are omitted on the ground that the student will see all these in the demonstrations and laboratory practice, and can learn much more under these conditions than from the best illustrations; while a certain amount of confusion, due to misinterpretation of the drawings and differences between the actual apparatus and the pictured, will be avoided. Pictures of different types of furnaces and of industrial equipment are quite incidental to the work, and can be studied to better advantage in an industrial chemistry, or shown and explained by the instructor by charts, lantern slides, or blackboard sketches.

An Appendix contains information in regard to the metric system and the measurement of temperatures, and also tables of specific gravities, solubilities, etc., for ready reference and comparison. A table of atomic weights will be found on the inside of the back cover.

J. T. S.

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INTRODUCTION TO GENERAL CHEMISTRY

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CHAPTER I

PRELIMINARY DISCUSSION

AMONG the substances familiar to us, some remain permanently unaltered, while others undergo more or less rapid transformations into quite different substances. Iron becomes rust; wood burns to ashes; food is digested and nourishes the body; seeds grow into plants; lime is made by heating limestone, and is "slaked" by water; and mortar, which is made by mixing the slaked lime with sand and water, gradually changes to a stonelike hardness. We know, too, that coke, tar, and gas are obtained from coal by heating it in retorts; and that iron, lead, and other useful metals are extracted from minerals.

The common characteristic of all these changes is that the original substances disappear with the production of other substances of totally different properties. It is with changes of this kind that chemistry has to do. Its object is to study the composition of substances, the conditions under which they may be produced, and under which they may be converted into others, with all the attendant phenomena.

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Changes which do not involve such complete and permanent alterations are called physical changes. Such are changes of place and all the phenomena of motion; changes of temperature, of form, and of volume; and changes in behavior due to magnetism and electricity.

Properties of Substances. — Most of our knowledge of a substance is expressed in a description of its properties, and each substance has certain properties by which it is recognized and identified. Among the very many properties which every substance has, a few of the more important for its identification are: its condition or "state," whether solid, liquid, or gas, at ordinary temperatures, and the temperature at which it changes from one state to another (melting and boiling points); its color, odor, and taste; its solubility in water and in other liquids; and its behavior toward known substances. These properties are always the same in all specimens of the same substance, whatever its source, when they are examined under the same conditions. Under different conditions, some of these properties may show marked differences: at different temperatures, the substance may be solid, liquid, or a gas; metals which are bright and lustrous in the compact state may be obtained in the form of dull, earthy, or black powders; transparent substances, like glass, become white opaque powders when pulverized, and, if colored, lose much of their color; the boiling point of a liquid varies with the pressure at which it is determined; and the solubility often varies very much with the temperature. The chemical behavior, too, differs widely under different conditions, especially those of temperature; many

chemical changes which do not occur at all at ordinary temperature, or so slowly as to escape notice, going on rapidly when the substances are heated. Odor, taste, and the melting points of solids are not subject to much variation; but it is evident that in our study of properties for purposes of identification careful attention must be paid in most cases to the conditions under which the observations are made.

All substances have the properties of **weight** and of **occupying space**. While this is at once obvious in the case of solids and liquids, it is not so immediately apparent in the case of gases. The fact that gases have weight and occupy space may, however, be readily demonstrated. If we weigh a flask fitted with a stop-cock, and which has been open to the air, and then withdraw most of the air by means of an air pump, the weight is found to be less. On allowing the air to enter the flask again, the former weight is restored. A gas which may be obtained by the action of hydrochloric acid on marble is so much heavier than air that it can be poured down through air much like water. If a cylinder containing this gas is inverted over a burning candle, the descent of the gas is shown by the going out of the candle; and if poured into a weighed beaker on a balance, its weight is at once apparent. Other gases, like illuminating gas, are lighter than air, so that they may be poured up through it, and if used to fill balloons, cause them to ascend.

That air occupies space is evident when one attempts to pour a liquid into a bottle through a closely fitting funnel, or plunges a tumbler mouth downward into water.

The weight of a body is a measure of its **mass** or the quantity of matter which it contains. While the mass of a given body remains unchanged, its weight, which is the pull of the earth on it, varies at different latitudes on account of the different distances from the center of the earth and the differences in centrifugal force due to the earth's rotation. These variations in weight, however, which would be shown by a spring balance, do not appear when an ordinary balance is used; for in this case the body is compared with standard masses (weights) which are subject to the same variations. Therefore, the weight of a body, found by means of a chemical balance, is a true measure of its mass; and we usually speak of weight rather than mass.

The space occupied by a given weight of a substance is by no means invariable, since all substances expand and contract with changes of temperature, and the volume of a gas is readily changed by changes in pressure. The relation of the weight of a body to the space it occupies is known as density or specific gravity. The terms are often used interchangeably ; but properly, **density** means *the weight of unit volume*, —the weight in grams of one cubic centimeter or liter; and **specific gravity**, *the ratio of the weight of a body to that of an equal volume of some substance which is taken as a standard*. In the case of solids and liquids the standard substance is water, while gases are usually compared with air. Since the volume of a body varies under different conditions, especially those of temperature, while the weight is unchanged, the density of a substance also varies, and for purposes of exact comparison, densities must be determined under like conditions.

The Conservation of Mass. — In this brief discussion of the properties of substances, it appears that mass measured by weight is the one property of a body which is not changed when conditions of place, temperature, or of pressure are altered. It has also been found that weight persists through all chemical transformations; that the weight of the products of a chemical action is invariably equal to the weight of the substances which take part in the change; or in other words, *matter can neither be created nor destroyed.* This fact is of the greatest importance, for it enables the chemist to follow matter through all of its changes and find the exact relations which exist between various substances.

It is true that in many instances, as in the burning of alcohol or a candle, there appear to be no weighable products, — there is a complete disappearance of the substance with the production of imponderable light and heat. A very simple experiment will, however, prove that this apparent destruction of matter is due to the fact that the products of the burning are invisible gases. If a burning candle is lowered into a large flask, and the mouth of the flask is closed, a fine mist appears on the glass, and the candle soon goes out. If we now remove the candle and shake a little limewater in the flask, it becomes milky. In a flask full of air, the limewater remains clear. We learn from this that air is necessary for the burning of the candle, and that there are at least two products from its combustion, — water, in the form of an invisible vapor which condenses to liquid on the cool glass, and a gas different from air, which turns limewater milky.

If an experiment is arranged so that the products of

the burning candle are absorbed in a solid substance while the candle is burning, it will be found that these products weigh more than the part of the candle which is burned up; for the products are formed by the chemical combination of the air necessary for the combustion and of the candle material, and their weight can be proved to be exactly equal to the weight of the candle material and of the air which have disappeared.

Elements. — From the almost endless variety of substances which are known, chemists have succeeded in extracting about eighty constituents, which appear to be of the simplest possible character.   They form other substances only by chemical union.   These simplest forms of matter are the chemical elements of which all other substances are composed.

LIST OF SOME COMMON ELEMENTARY SUBSTANCES

Aluminium	Magnesium	Tin
Copper	Mercury	Zinc
Gold	Nickel	Carbon
Iron	Platinum	Phosphorus
Lead	Silver	Sulphur

Some of these elementary substances we shall use in our first study of other substances, as well as sodium, a metal which is not in common use.

A full list of the elements which are known will be found on the back cover of this book.   The greater number of them are of a metallic character, as is the case in the short list just given.   There are, in fact, only eighteen elements of a distinctively non-metallic appearance and behavior, and of these, ten are gases.

Only four of the elementary substances are liquid at ordinary temperatures, — three metals and one non-metal, sixty-six being solids. Only a few of the elements occur uncombined, or free, in nature, most of them being in combination as chemical compounds. Many of them are found in very small amounts, and a number are very rare. A table in the Appendix shows the relative abundance of the elements, as computed by Professor F. W. Clarke.

Very many compounds which do not occur naturally are made in the laboratory and in chemical industries.

Compounds. — *Every definite chemical compound always contains the same elements in the same proportions by weight*. This fact has been established as the result of innumerable determinations in which the compounds have been analyzed, — separated into their constituents; and synthesized, — formed from their constituents. It holds good whatever the source of the compound or the method of its formation. With this constancy in composition goes a similar constancy in all of the properties which characterize the compound. Most of these properties are entirely different from those of the constituents; common salt offers no suggestion that it is composed of elements which by themselves are a suffocating and ill-smelling gas, and a light metal which acts vigorously on cold water; and in the gas which turns limewater milky, there is no indication of a constituent which, in the free state, is known in various forms, as charcoal, graphite, and diamond.

Mixtures. — Many substances are not single, definite compounds, but mixtures of compounds or of elementary substances, or of both. In these the components may

often be present in any proportion. Before the com-
position of a compound can be determined, and fre-
quently before the compound can be identified, it must
be separated from any admixed substances. This is
accomplished by taking advantage of the fact that in a
mixture the properties of the components remain the
same. In the case of solids, when the particles are too
small to be sorted by hand, the components may be
separated by methods depending on their differences in
properties. Differences in solubility are very fre-
quently employed for this purpose. For instance, the
three components of gunpowder may be separated by
dissolving the saltpeter in water, and then the sulphur
in carbon disulphide. The charcoal is left undissolved,
and the saltpeter and sulphur are recovered in solid
condition by the evaporation of their solvents. When
two or more solid compounds are together in solution,
they may often be separated by slow evaporation, the
least soluble crystallizing out first, and so on. Mixtures
of liquids may be more or less completely separated by
distillation, the more volatile going over first. Often
the crystallization or the distillation has to be repeated
several times before the individual compounds are ob-
tained in a pure state. Gases are usually separated by
absorption in various substances.

Pure Compounds. — A pure chemical compound which
is solid is usually distinguished from an impure com-
pound or mixture by its sharply defined melting point,
if it melts without chemical change ; pure liquid com-
pounds are characterized by having a constant boiling
point ; pure gases, by their complete absorption or
non-absorption in different substances ; and all pure

substances, by the character of the new compounds they form with known substances.

When a substance has been obtained in a state of purity, the constituent elements are identified by a series of experiments, and the proportions in which they are present are ascertained. With these facts as a basis, the chemical behavior of the substance toward other substances can be studied and interpreted.

Necessity of Experiment. — While a considerable number of chemical facts may be learned by watching everyday occurrences, we should not progress very rapidly or very far in our knowledge of chemical phenomena if limited to such observations. We have seen how much can be learned about combustion by simple experiments with a candle; similarly, by properly planned experiments, we can not only discover the character of chemical changes, but can cause many chemical transformations to take place, which would never occur of themselves, and thus very greatly extend and coördinate our knowledge.

Laws and Theories. — When the facts which are learned by observation and experiment are classified, it will be found that certain general statements may be made which express and sum up in a concise form whole groups of facts and their relation to each other. Such a statement is called a **law**. In the sense in which it is used in science, the word carries no meaning of obligation to authority, as in the usual use of the term, and such expressions as "obeys the law" should be avoided. The facts are independent of the law; the law is simply a convenient summary of them. It is a law that all

forms of matter have weight and occupy space; that matter is indestructible; that a chemical compound is always composed of the same elements in the same proportion by weight,— simply because these are the facts which have been found by all our experience. If facts should at any time be found which do not agree with these statements, they could not be compelled to obey the laws, but the laws would have to be qualified or changed.

When we attempt to explain the facts which are found,—for the mind is always seeking for explanations — we picture to ourselves certain possibilities which might account for the phenomena, that is, we make **hypotheses**. These are tested by a careful survey of the known facts, and by the attempt to discover new facts which may be suggested by the hypotheses. The hypotheses which stand these tests successfully take rank as **theories**. Those which fail are, of course, discarded, and even theories have to be modified or given up in the light of new facts. Some theories are so well established, and are sometimes presented in such a positive manner, that the student is in danger of feeling that they are assured facts. It is, therefore, important to keep the facts, which are unalterable, distinct from the theoretical explanations, which are liable to change. Hypotheses and theories not only provide the explanations of phenomena which the mind demands, but have been, and are, of greatest value as a stimulus to the discovery of new facts.

The order of scientific method is, then : first, the establishment of facts by observation and experiment; second, the classification of these facts and the formu-

lation of laws; third, the attempt at explanation by
hypotheses; fourth, the testing of hypotheses.

Chemistry is a well-organized science with a multitude
of recorded facts, many well-established laws, and some
satisfactory theories. These may all be found, explic-
itly and accurately given, in chemical treatises. The only
way, however, by which the subject becomes real and vivid
is through personal experiment. Moreover, the advan-
tage of a first course in chemistry does not lie so much
in the acquisition of facts as in learning how to use
the scientific method, and to gain the scientific point of
view. To know how to observe, how to experiment,
and how to reason logically from the observed facts,
gives a training which is of service in all study and in
all the activities of life. Chemistry has a peculiar value
as a means for such training, on account of the great
variety of experimental work which it offers, and the
great interest of its subject matter.

CHAPTER II

THE COMPOSITION OF AIR

IT is a well-known fact that ordinary air always contains moisture in the form of invisible vapor, and that this is present in varying amounts. Under usual circumstances, however, the moisture amounts to not more than one per cent of the weight of the air and will not seriously disturb our attempts to discover the other constituents.

Is air an elementary substance? We may answer this question by finding out by experiment whether a given quantity of air will all combine with some known elementary substance to form a single compound. A preliminary study of the behavior of some of the commoner elementary substances when heated in air will help us to select those best fitted for our purpose. Some metals, such as gold and platinum, are unaltered in air at any temperature, while a number of other metals, such as iron, lead, tin, zinc, copper, magnesium, and sodium, are changed, more or less rapidly, when heated, into solid compounds. Carbon and sulphur burn with the formation of gaseous products. Phosphorus ignites readily and burns with the production of a white smoke, which is very soluble in water. Even at ordinary temperatures, air acts slowly on phosphorus.

As our experiment is to decide whether all or only

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part of the air takes part in combustion, the element most suitable is one which gives a solid product. In this the gas will disappear; while a gaseous product, taking the place of the air by whose action it is formed, would leave us in doubt, unless it could be absorbed in some liquid. Phosphorus and copper are perhaps the best elements to use.

Analysis of Air.[1] — If a piece of phosphorus is ignited in air enclosed in a bell jar over water, we find that only about one fifth of the air disappears, no matter how much phosphorus we use. As phosphorus acts on air at ordinary temperatures, we may repeat the experiment in different form by bringing a piece of phosphorus on the end of a wire into a measured volume of air in a tube closed at one end, standing with its open end in water. The action in this case is much slower, but at the end of several hours we shall find, on measuring the gas which is left, that its volume is about four fifths of the original volume of air. Further, if we arrange an experiment so that a measured volume of air is passed slowly through a tube containing heated copper, and any gas which escapes the action of the copper can be collected for measurement over water, we shall find again that the same proportion of air as before remains unaffected.

We may conclude, therefore, that the air is not an elementary substance, but contains at least two dissimilar constituents, one of which is the active agent in supporting combustions, while the other or others play no part in these phenomena. The indifferent gas which makes up four fifths of the volume of the air was con-

[1] Stoddard's "Quantitative Experiments," pages 39–41.

sidered for over a hundred years to be a single elemen-
tary substance, — **nitrogen**; but in 1895 it was discovered
that it contained, mixed with it, a small amount of a
still more indifferent gas, which was named argon; and
it has since been found that this argon, in turn, is a
mixture of argon and four other similar gases, helium,
neon, krypton, and xenon.

The Active Constituent of Air. — While the indifferent
gases of the air are readily obtained by themselves by
the removal of the active constituent, we are unable to
find any substance which will combine with these gases
and leave the active gas for examination. There are,
however, several substances which unite with this gas
at one temperature and part with it at a higher tempera-
ture, and which, therefore, may be used for its indirect
preparation from the air. A classic experiment of this
kind is one made by the French chemist, Lavoisier, who
found that mercury, when heated in air to a temperature
a little below its boiling point, was slowly changed into
a red powder which separated into mercury and gas on
being strongly heated by itself. This and other methods
of a similar character cannot, however, be easily carried
out by the student; but a gas which may be obtained
from a number of different substances can be identified
with the active gas in the air by the fact that certain
compounds which they form are alike in every respect.

Mercuric oxide, red lead, potassium chlorate, manga-
nese dioxide, potassium permanganate, all give, on heat-
ing, a gas which rekindles a glowing splinter of wood, and
in which many substances burn most vigorously. This
gas is the elementary substance known as **oxygen**. If we
prepare this gas and compare the products formed by

burning substances in it with the products which the same substances yield when burned in air, we shall find that they are identical. Phosphorus gives in both a white smoke which is very soluble in water, imparting to the water a sour taste and the property of turning litmus paper red; sulphur burns in air and in oxygen with the production of a suffocating gas of characteristic odor, whose solution in water is also acid and reddens litmus; carbon burns to a gas which extinguishes flame and turns limewater milky; copper is changed to a black substance which appears the same in both cases; magnesium is converted into a white powder which turns moistened litmus paper blue. The most critical examination would show that in all these cases the products are exactly the same in composition and in properties. The chemically active gas of the air is, therefore, oxygen.

Is air a chemical compound or a mixture? — We can draw no conclusion in regard to this from the experiments we have made, for in a chemical reaction one constituent can be withdrawn from a compound as well as from a mixture. But an examination of the properties of air shows that they are what we should expect from a mixture of the components, and not the new set of properties which are characteristic of a chemical compound. Air is slightly soluble in water, and when it is expelled from this solution by heating, the proportions of the gases are changed; this is unlike the behavior of a compound, which always has the same composition when recovered from solution. When liquid air boils, it does not act like a compound, which would give a vapor or gas of the same composition as the liquid, but

loses nitrogen more rapidly than oxygen, so that the last portions are almost pure oxygen. The density of air and all of its ordinary physical properties are exactly those which can be calculated from the properties of its components when mixed in the proportions in which they are found in air. Also, when oxygen and nitrogen are mixed in these proportions, although there is no evidence of chemical action, such as the production of heat or change of volume, the mixture behaves in every respect like ordinary air. *Air is, therefore, a mixture of its component gases*, and from the chemical point of view may be regarded as oxygen so diluted by the large admixture of indifferent nitrogen gases that the phenomena of combustion are much modified in their intensity, and under a control which would be impossible in pure oxygen.

Besides these chief components of air, there is always present a small but nearly constant amount of the gas which results from burning carbon, called **carbon dioxide**. Since all of our fuels contain carbon, this gas is poured into the air in enormous quantities ; but in spite of this fact, the proportion of carbon dioxide in the open air of the country has always been found to remain practically unchanged, and to amount to about three parts in 10,000 of air. The explanation of this is that vegetation utilizes this gas for its growth, appropriating the carbon to build up its structure, and returning the greater part of the oxygen to the air. As plant growth is stimulated by an increase in the proportion of this gas, an almost perfect equilibrium is maintained.

Water vapor is always present in ordinary air as the result of the evaporation which goes on at all temperatures. Under certain conditions it becomes visible in

clouds and fogs, and is precipitated as rain or snow. The moisture of the air is also condensed to liquid form on surfaces which are sufficiently cooled, as on a tumbler of ice water, or on grass at night, disappearing again when the temperature rises. The amount of moisture which air can contain is evidently greater when the air is warm than when it is cold. A study of the matter shows that at any given temperature air can hold any amount of vapor up to a certain proportion. When this maximum amount is present, the air is "saturated" with moisture, and when the air is cooled, some of the moisture must separate as water. Air saturated at 0° C. contains 4.9 grams of vapor in each liter; at 20°, 17.2 grams; at 30°, 30.1 grams. The proportion of moisture in the air is usually considerably less than the maximum: in winter, in a furnace-heated house, it may be only 20 per cent of this amount; in summer dog days, 80 to 90 per cent, rising to 100 per cent in a storm.

Other gases and vapors, and dust, are usually found in air in small and varying amounts.

The proportions of oxygen and the nitrogen gases in air is very nearly the same in all parts of the world on account of the rapid diffusion of the gases into each other and the constant movement of the air. The following table gives the **average composition of air** deprived of carbon dioxide, moisture, and other variable components:

	By Volume	By Weight
Nitrogen	78.16	75.54
Argon gases	0.94	1.44
Oxygen	20.90	23.02
	100.00	100.00

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The differences in the figures in the two columns show that oxygen and the argon gases are denser than nitrogen.

The **pressure** due to the weight of the air is measured by the height of the column of mercury which it sustains in the barometer (p. 19). Barometer readings show that this pressure is almost constantly varying. One of the causes of these variations is the varying amount of water vapor in the air. Water vapor is much lighter than the other gases of the air, and as it occupies the same space as any other gas, moist air is lighter than dry air, and lighter as the proportion of water vapor is greater.

Atmospheric Pressure.— The weight of the air produces pressure on all surfaces with which it is in contact. This fact becomes evident when the air is partly or wholly removed from one side of an object, as when a piece of sheet rubber is placed over the receiver of an air pump, or when a tube closed at one end is filled with water or mercury and placed with its open end in the same liquid. The liquid is sustained in the tube, filling it completely if the vertical height of the tube does not exceed a certain value which depends on the specific gravity of the liquid, or falling from the top of the tube to a certain level if the height of the tube is greater. It is found that the vertical height of a column of water which balances the atmospheric pressure is about 34 feet, and that of mercury about 30 inches or 76 centimeters. This corresponds to a pressure of about 15 pounds on each square inch of surface, or something more than one kilogram on each square centimeter.

The chemist makes frequent use of atmospheric pres-

sure in the manipulation of gases. Vessels filled with water are inverted in water, and then the water is displaced by a gas. In this way gases are conveniently collected for experiments. In the case of gases soluble in water, mercury may be employed instead of water.

The barometer is a tube in which mercury is sustained by the pressure of the air in the manner which has been described. The tube is longer than the column of mercury so that this is free to rise or fall with changes of pressure, the space above the mercury being a vacuum. In reading the barometer, it is important that it hang vertically, as any inclination increases the length of the column. Since the pressure of the air is subject to frequent changes, and since variations in pressure affect the volume of gases, a knowledge of the pressure (barometric height) at which a volume of gas is measured is important in comparing gas volumes and in determining the exact quantity of a gas in a given volume (p. 22).

The Weight of Air. — The weight of a measured volume of air may be roughly found as follows : A flask full of air is weighed, and after most of the air has been withdrawn by an air pump it is weighed again. Water is then allowed to enter the flask until no more comes in, and this water is measured. The volume of water is equal to the volume of the air which was withdrawn from the flask, and whose weight is the difference of the weights of the flask.[1]

Exact experiments have shown that a liter of pure, dry air weighs 1.293 grams under standard conditions (p. 22).

[1] "Quantitative Experiments," page 25.

CHAPTER III

THE MEASUREMENT OF GASES AND THE MOLEC-
ULAR CONSTITUTION OF MATTER

Solid bodies have definite forms and volumes. **Liquids** have a definite volume, but the form is that of the vessel in which they stand. **Gases**, however, tend to expand indefinitely and fill any space offered them, and thus the volume as well as the form of a gas is that of the space in which it is contained. Solids and liquids are changed very little by pressure, but gases may be readily compressed to a very small volume, and must be under some pressure so long as they have measurable volumes.

The Gas Laws. — It has been found that all gases behave very nearly alike when the pressure is changed, and this uniform behavior is expressed in the statement known as **Boyle's Law**: *The volume of a gas is inversely proportional to the pressure under which it stands.*[1]

The volume of solids, liquids, and gases is different at different temperatures; but while the ratio or **coefficient of expansion** of liquids and solids is peculiar to each substance, all gases expand and contract equally for the same change in temperature. If we express

[1] " Quantitative Experiments," page 16.

temperatures on the scale of the centigrade thermometer (see Appendix), which is almost always used in scientific work, the volume changes $\frac{1}{273}$ of its value at 0° for every degree through which the temperature rises or falls; so that if the volume at 0° is 273 cc., it would become 288 cc. at 15°, 373 cc. at 100°, or 223 cc. at − 50°. If it were possible to cool a gas down to − 273°, and it followed this law in its contraction, the volume would be zero, — that is, the gas would entirely disappear. As a matter of fact, all gases are known to become liquids before this temperature is reached; but this theoretical result of the law indicates − 273° as the lowest conceivable temperature. It is, consequently, called the **absolute zero** of temperature, and temperatures reckoned from it in centigrade degrees are called **absolute temperatures**. On this scale, 0° centigrade would be 273°, and any temperature given in centigrade degrees is changed to the corresponding absolute temperature by adding 273.

The law which expresses the relation between the volume of a gas and the temperature is known as **Charles' Law**, and may now be given this simple statement: *The volume of a gas is proportional to its absolute temperature.*[1] If a gas is heated in a closed vessel so that it cannot expand, it is found that *the pressure increases in proportion to the increase in absolute temperature.*[2] This is readily seen to be in accordance with the laws of Boyle and of Charles.

These laws for the relation of the volume, pressure, and temperature of a given quantity of gas may be all expressed in algebraic form as follows, where V is the

[1] *Ibid.*, pages 19–21. [2] *Ibid.*, page 22.

volume, P the pressure, and T the absolute temperature:

$$\frac{PV}{T} = \text{a constant value.}$$

If T remains unchanged, P must vary inversely as V (Boyle's law); if P is constant, V and T must vary in the same ratio (Charles' law); and finally if V is kept the same, P must vary in the same ratio as T.

Measurement of Gases. — Gases are usually measured in closed flasks or tubes or other vessels of glass in which the gas is cut off from the air by a water or mercury seal, the tube standing mouth down in a dish of water or of mercury. If the liquid stands at the same level within and without the tube, the gas is then under the pressure of the atmosphere. This is measured by the height of the mercury column in a barometer, and is usually spoken of as the **barometric pressure.**

Because of the considerable influence which temperature and pressure have on the volume of gases, it is evident that when gaseous volumes are measured for the purpose of comparison, or as a means of determining the weight of the gas from the known weight of the unit volume, the measurements would not be of much value unless both temperature and pressure at the same time of measuring were taken into account. In practice we calculate by the aid of the laws of Charles and of Boyle what the measured volume would be at 0° C. and under a pressure of 760 mm. of mercury in the barometer, these being adopted as standard or "normal" conditions, and use the **normal volumes** thus obtained. The application of the laws in finding the

normal volume of a gas is very simple. The corrections for temperature and for pressure may be made successively in either order, or we may use a formula in which both corrections are combined.

Correction for Temperature. — Since the volume is proportional to the absolute temperature, and absolute temperature is equal to the centigrade temperature plus 273, if t represents the reading of the thermometer when the gas was measured, v the volume, and v_0 the volume at $0°$ C.,

$$v_0 : v : : 273 : 273 + t, \quad \text{whence,}$$

$$v_0 = v \frac{273}{273 + t} = v \frac{1}{1 + 0.00366\,t}.$$

Correction for Pressure. — If v is the volume of gas to be corrected, b the pressure (usually the barometer reading at the time of measurement), and v_{760} the volume at 760 mm., then according to Boyle's law:

$$v_{760} : v : : b : 760, \quad \text{whence}$$

$$v_{760} = v \frac{b}{760}.$$

If the gas stands over water, it is saturated with water vapor, and the pressure of this vapor makes the volume greater than it would be if the gas were dry. The value of this pressure, or "aqueous tension," depends solely on the temperature of the water, and may be found in the table of "Aqueous Tensions" (Appendix). The volume of the dry gas at the barometric pressure of the experiment may be calculated by Boyle's law: If b is the barometric pressure, w the aqueous ten-

sion, v the measured volume, and v_d the volume of the dry gas,

$$v_d : v :: b - w : b, \text{ or } v_d = v - v\frac{w}{b}.$$

Usually, however, the corrections for aqueous tension and for barometric pressure are made in one operation by use of the formula:

$$v_{760} = v\frac{b - w}{760}.$$

Finally, the corrections for temperature, for pressure, and for aqueous tension may be all included in the following formula, in which v_n is the normal volume of the dry gas:

$$v_n = v\frac{273\,(b - w)}{760\,(273 + t)}, \text{ or } v_n = \frac{b - w}{760\,(1 + 0.00366\,t)}.$$

Diffusion of Gases. — In addition to the facts about gases expressed in the gas laws which we have discussed, it is important to notice that gases tend to mix or diffuse into each other. Whenever two gases are brought together, diffusion begins and goes on continuously till they are uniformly mixed. Even when the gases are very different in density and the heavier is placed below the lighter, the lighter finds its way down into the heavier and the heavier up into the lighter, against the action of gravity. As illustrations of diffusion, we may note the spread of odors through the air, and the uniform mixture of gases in the atmosphere. Once mixed, there is no tendency to separate, as by the settling out of the heavier gas.

The rates of diffusion of different gases have been

experimentally determined, and it is found that they are inversely as the square root of the gas densities. If, for instance, two gases, one of which is sixteen times as dense as the other, are separated by a porous partition, the lighter gas will pass through the partition four times as rapidly as the heavier passes into the lighter.

The Kinetic-Molecular Theory.[1] — All these facts about the behavior of gases, and many others, are explained by the **molecular theory of gases**. According to this theory, a gas is pictured as consisting of very minute particles, called **molecules**, which are all alike. The size of the molecules is far beyond the highest power of the microscope ; they are not only not in contact with each other, but are separated by distances which are very great as compared with their size. One cubic centimeter of gas is estimated to contain a number so great that it is expressed by 7 followed by twenty ciphers. There is no sensible attraction between the molecules, and they are supposed to be perfectly elastic. They are in continuous and very rapid motion, moving in straight lines, colliding with each other and with the walls of the vessel which contains the gas, and rebounding. The velocity of this motion is not the same for all of the molecules at any given time, but the average velocity remains constant so long as the temperature is unchanged ; when the temperature is raised, this average velocity is increased, and becomes less when the temperature is lowered. Temperature, indeed, is considered to be a consequence of the molecular motion

[1] Cf. Risteen's "Molecules and the Molecular Theory " ; and Walker's "Introduction to Physical Chemistry," 3d edition, page 89.

and an expression of the **kinetic energy** of the molecules.
Kinetic energy, or the energy of the mass in motion, is
equal to the product of the mass by the square of the
velocity; and the kinetic energy of the molecules is
proportional to the absolute temperature. At the ab-
solute zero, therefore, all motion would cease, and all
kinetic energy disappear.

Now let us see how this theory explains the observed
facts in regard to gases. In the first place, the diffu-
sion of gases is a direct consequence of the molecular
motion ; and the rate of this diffusion may be used as
a measure of the molecular velocities, which are, there-
fore, inversely as the square roots of the densities.

The pressure exerted by a gas is the result of the
ceaseless and inconceivably rapid succession of blows
which the walls of the containing vessel receive from
the impacts of the molecules. If a given volume of
gas is reduced to one half by pressure, the molecules
will be half as far apart as before and will have only
half as far to go before striking the walls ; and if the
temperature and, consequently, the average velocity
remain the same, the number of impacts in a given time
will be doubled, and the pressure twice the original
amount. Similar reasoning for different volumes gives
the law of Boyle.

When the temperature of a gas is raised, according
to the theory the velocity of the molecular motion is
increased. This results in a more rapid bombardment
of the walls of the vessel and a greater volume if the
pressure is kept constant, or a greater pressure if the
volume is constant. The relation of the temperature
to the volume or the pressure is found in the statement

that the kinetic molecular energy is proportional to the absolute temperature.

It also follows from the theory that *equal volumes of all gases under similar conditions of temperature and pressure contain equal numbers of molecules.*[1] This same conclusion is also reached from purely chemical considerations, quite apart from the gas theory, and is known as the **hypothesis of Avogadro.**

In this discussion of the molecular theory of gases and of the explanation it gives of the laws of Boyle and of Charles, no account is taken of the space occupied by the molecules or of any attraction which they may have for each other. The molecules must, however, occupy some space, and there must be some intrinsic attraction between the molecules, since all gases can be condensed to liquids in which the molecules cohere. Only in an ideal or perfect gas in which the molecules are physical points and without mutual attraction would the behavior of gases exactly agree with the gas laws. If the molecules occupy a sensible part of the gas volume, the volume would decrease less rapidly under increased pressure than is stated in the law of Boyle ; while the attraction of the molecules would aid the pressure and tend to produce a less volume than accords with the law. As the gas by the application of cold or pressure approaches the state of liquid, we should expect the influence of the attraction to increase. These opposite influences unless exactly balanced would cause deviations from the laws. As a matter of fact, none of the gases are found to behave precisely as stated in the gas

[1] *Cf.* Walker's "Introduction to Physical Chemistry," 3d edition, page 91.

laws, but under ordinary conditions the agreement is sufficiently exact to serve for most purposes of measurement and comparison.

Liquefaction of Gases. — All known gases have been liquefied by cold or pressure or by both. It is found that there is for each gas a certain temperature above which no amount of pressure can change it to a liquid. This is called the **critical temperature** of the gas, and may also be termed the **absolute boiling point** of the substance, since at this temperature the liquid is converted into vapor or gas no matter how great the pressure may be. The critical temperature of oxygen, for instance, is $-119°$, that of water, $365°$.

Constitution of Solids and Liquids. — Solids and liquids are also supposed to consist of molecules which are not in contact with each other, and which are in motion, though the motion is quite different from that of the gas molecules and much more circumscribed.

The facts that all kinds of matter can be compressed; that they expand and contract with changes of temperature; that liquids as well as gases diffuse into each other, a heavier liquid diffusing into a lighter placed on top of it, until, in course of time, a homogeneous mixture results; that the volume of a solution is usually less than the sum of the volumes of the solvent and the dissolved substance, — all these facts, and others, agree with the molecular conception of matter.

The molecule has a special significance for the chemist, for it is regarded as the smallest possible portion of a substance which retains or can retain the essential properties of the substance.

CHAPTER IV

WATER AND ITS COMPOSITION

WATER is found everywhere and in great abundance. It covers about three quarters of the earth, and is always present in the soil and in the air. Animals and plants contain considerable quantities, and it is essential to their life. It condenses on all surfaces, so that all substances are covered with a very thin film of moisture, and for accurate weighing must be carefully dried.

If we evaporate some tap water in a porcelain dish, we shall find that a small amount of residue is left. This consists of solid substances which the water has dissolved from the earth with which it has been in contact. If we heat this residue, it often darkens, gives an odor of burning, and finally becomes white. The darkening is due to the charring of organic substances from dead leaves, etc., while the final white residue consists of mineral or inorganic substances which were dissolved from the rocks and soil. Water from different sources contains very different amounts of solid matter in solution. Rain water collected before it reaches the ground, or water from melted snow, is the purest form of natural water; for in the evaporation from surface waters, the water vapor which is finally condensed to clouds and rain leaves behind all of the substances which were in solution.

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When a glass of freshly drawn water stands in a warm room, we notice, after a time, bubbles of gas adhering to the sides of the glass. This gas consists of the gases of the atmosphere, which, as we have seen, are somewhat soluble in water.

Pure Water. — On boiling ordinary water, the gases dissolved in it are expelled, and when the steam is condensed by passing through a tube kept cool by a water jacket, we obtain **distilled water**, free from the substances which were in the boiling water, and from most of the gases. This process of distillation is essentially like that by which rain water is produced in nature, and is employed to provide the pure water used in chemical laboratories and for other uses. Distilled water is not, however, absolutely pure, for the solvent power of water is so great that minute amounts of almost everything with which it comes in contact, such as the glass of the flask which holds it, are dissolved; but the impurity is so very slight that distilled water serves for all usual chemical purposes.

Physical Properties and Uses of Water. — Most liquids, when heated, expand more or less regularly from their freezing point until they boil. Water presents an interesting exception to the rule. If ice water is heated, it first contracts up to about 4°, and then expands as the temperature rises, till at 100° it changes into steam. When water is cooled, therefore, it expands as it nears the freezing point; and in a pond when heat is lost chiefly at the surface, it floats on the warmer but heavier water beneath. Water expands again in freezing, the ice occupying a volume about nine per cent greater than the water, so that the ice formed on top

of the pond remains there. This fact is readily seen to be of great importance in nature. Water at its point of least volume and greatest density serves as the standard for the metric system of weights and measures; one cubic centimeter of water at 4°, the point of its greatest density, weighs one gram. The specific gravity of solids and liquids is expressed with reference to water as unity, at some specified temperature. The **specific heat** of substances — the quantity of heat necessary to change the temperature of one gram through one degree centigrade — is determined with reference to the specific heat of water as the thermal unit.

Melting Point. — The melting temperature of ice, which remains constant so long as water and ice are in contact, fixes the "freezing point" on thermometers, — 0° on the centigrade scale, or 32° on the Fahrenheit. Water does not, however, invariably freeze when its temperature is brought to 0°. It is possible to cool it several degrees below this point without the formation of ice, but the cold water immediately freezes when touched with a piece of ice, and the temperature rises at the same time to 0°. Other substances behave in the same way; and hence the *freezing point of a liquid is defined as the temperature at which the solid and liquid are in equilibrium with each other*, — that is, when both, in contact with each other, have the same temperature.

Boiling Point. — The temperature at which water boils under the atmospheric pressure of 760 mm. of mercury determines the boiling point of thermometers, 100° C., or 212° F. The boiling point of water (and of other liquids) is quite dependent on the pressure against which the vapor has to make its way. Under a pres-

sure of 190 mm. ($\frac{1}{4}$ atmosphere) the boiling point is about 65°, and with 1520 mm. pressure (2 atmospheres), water boils at 123.° As we have had occasion to note (p. 16), water evaporates at all temperatures, and produces a vapor tension which increases as the temperature is higher. When this tension becomes equal to the pressure which is opposed to it (usually the atmospheric pressure) the water boils. We may, therefore, describe the *boiling point of a liquid as the temperature at which its vapor tension is equal to the atmospheric pressure.*

Water has the highest **specific heat** of any known substance. In changing from water to ice, 80 thermal units are set free, and the same amount disappears when ice melts ("heat of fusion"). That is, one gram of water at 0°, in freezing to ice of the same temperature, gives off enough heat to change the temperature of a gram of water from 0° to 80°. To convert water at 100° into steam, also at 100°, requires 537 thermal units, and in the reverse change, the same amount is set free ("heat of vaporization"). These facts are explanatory of the influence which large bodies of water have in regulating changes of air temperatures, and of the effectiveness of steam for heating purposes.

Water as a Solvent. — We have already had occasion to notice that water dissolves a great many substances. Sea water, which collects the drainage of the world, must contain every soluble substance, many of them, of course, in very minute quantities. The solubility of substances varies between wide limits, and usually depends largely on the temperature. When a solid is shaken in water till no more dissolves, the solution is

said to be saturated, and the amount of substance which can be dissolved in 100 parts of water is called the solubility of the substance at the temperature of the experiment. When a saturated solution is cooled, or some of the solvent evaporated, part of the dissolved substance usually crystallizes out. Some saturated solutions, however, when cooled, deposit no crystals and become **supersaturated**. This is an unstable condition, and can only occur when none of the dissolved substance is present in solid form. On adding a fragment of the solid, this becomes the center of a crystallization which goes on till the solution is just saturated at the existing temperature.

As a rule, the solubility of solids increases with the temperature, but the increase varies very much with different substances. Thus 100 grams of water dissolves 35.7 grams of common salt at 0° and 40 grams at 100°; while the same quantity of water will hold in solution 13.3 grams of saltpeter at 0° and 246 grams at 100°. In a few exceptional cases, the solubility is less in the warmer water, or increases up to a certain temperature, and then decreases. (*Cf.* solubility table in the Appendix.)

Some liquids, like alcohol and glycerine, mix with water in all proportions, giving homogeneous solutions. Others, after being shaken with water, separate and form a layer distinct from the water. This is the case with ether, chloroform, and kerosene for instance; but while the kerosene proves to be practically insoluble in water, and water in it, water and ether, and water and chloroform, dissolve in each other to a small amount. The solubility of liquids is influenced by temperature.

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Gases differ very much in their solubility in water. The gases of the air are very slightly soluble; some other gases dissolve freely, — 1299 volumes of ammonia, for instance, dissolve in one volume of water at 0°, and 710 volumes in one volume at 20°. Gases, as this illustration indicates, are less soluble in warm water than in cold, and the gas can usually be all driven out of solution by boiling.

Crystallization. — When the water of a saturated solution of a solid is partly lost by evaporation, or when a hot solution is cooled, some of the solid must separate or the solution will become supersaturated. The separation usually occurs, and in most cases the solid takes a crystalline form which is different with different substances. The crystals are small if the separation takes place rapidly, or if the solution is vigorously stirred during the crystallization, but may grow to a considerable size if the quiet solution is left to spontaneous evaporation.

A large number of substances combine with definite amounts of water in crystallizing, forming **hydrates**. The water contained in these hydrates is usually called **water of crystallization**. It is driven off from the crystals in most cases by moderate heating, leaving the **anhydrous** substance. The amount of water in the hydrates is sometimes large, — blue vitriol containing 36.07 per cent, and washing soda crystals, 62.96 per cent.

When the water of crystallization is removed, the crystalline form is destroyed, and colored crystals lose their color. Some hydrates lose part or all of their water when exposed to the air at ordinary temperatures. They are said to be **efflorescent**. On the other hand,

some solids absorb moisture so greedily from the air, that they finally pass into solution. Such substances are called **deliquescent**. They are employed by the chemist to dry gases by leading the gases through tubes filled with the substance, and to remove the moisture from solids by inclosing the solid and the deliquescent substance in a jar. Calcium chloride is commonly used for this purpose.

Chemical Properties of Water. — Water is a very stable compound, as is shown by the fact that only at a very high temperature — 2500° — is it decomposed into its constituents. Liquid water is, on the whole, an indifferent substance chemically, not reacting to any extent with the majority of other chemical elements or compounds ; so that solutions in water are very commonly used as a means of bringing about reaction between the dissolved substances, the water serving only as a convenient medium in which the substances may come into the intimate contact necessary for chemical change. In a number of cases, however, water enters into reaction with other substances, as in the slaking of lime; and in solutions, the water sometimes produces chemical changes. Such a change is said to be due to **hydrolysis**.

Analysis of Water. — If a slow current of steam is passed through a hard glass tube in which a piece of magnesium ribbon has been placed, and the spot where the magnesium lies is strongly heated, the metal will ignite and burn vividly to a white ash. At the same time, it will be found that a gas issues from the tube which will burn with an almost colorless flame. A comparison of the magnesium ash with the oxide of magnesium produced by burning magnesium in air or oxygen

will prove that they are identical.   Both have the same appearance, and both, when brought with a drop of water on to red litmus paper, turn it blue (**alkaline reaction**).   Other tests which we are not now prepared to make would establish the complete identity.   As the air was effectually cut off from the heated magnesium by the current of steam, we must conclude that water (steam) contains the element oxygen, in chemical combination with the gas which was set free in the experiment.

A somewhat similar experiment in which the reaction is under better control will enable us to collect the gaseous product in a cylinder over water and examine it. In this experiment steam is passed through a hard glass or iron tube which is partly filled with clean iron filings. After the steam has driven out the air in the apparatus, it condenses completely in the water at the end of the delivery tube; but when the iron is heated, a gas appears which is insoluble in water and may be collected in the cylinder.   An examination of this gas shows that it is combustible, — burning, as we saw in the magnesium experiment, with a nearly colorless flame; and it is very light, — escaping quickly from the cylinder when it is held mouth upward, and slowly when the cylinder is inverted.   This gas is **hydrogen**, one of the elementary substances.   The iron in the experiment is oxidized, though the change is not so evident as in the case of the magnesium.

A third set of experiments will serve to check the others.   If a small piece of the elementary substance, sodium, is dropped on to water in a dish, it will immediately melt into a globule and swim about on the water, with evidence of chemical action, growing smaller

and finally disappearing. During the action, a gas is given off which burns with a yellow flame when a lighted match is brought near the sodium. If we ram some sodium into a short tube, closed at one end, and bring it into the water, or place in the water a lump of sodium amalgam (p.244), the reaction will go on at the bottom of the dish, and the gas may be collected in an inverted test tube full of water. It is readily proved to be the same gas as that set free from the steam by iron. If we examine the water on which the sodium has acted, we will find that it has a soapy feeling and an alkaline reaction, turning red litmus paper blue. Now if some sodium is burned in an iron crucible in air, and the product brought into water, we shall find that the water has acquired the same properties as in the direct action of sodium. In the latter instance, the sodium reacted with a small portion of the water and the product was dissolved in the rest; in the former, the sodium reacted with the oxygen of the air, and the product was dissolved in water. As we have the same end result, it is evident that air and water contain one common constituent, — **oxygen**.

These experiments prove that hydrogen and oxygen are constituents of water. While it would also appear probable that these are the only constituents of water, these **analytical** results ought to be checked by a **synthesis**, — by seeing if water can be formed by a union of hydrogen and oxygen alone.

Synthesis of Water. — Hydrogen is made for experimental purposes by the action of zinc on dilute sulphuric acid. The first portions of gas are rejected because the hydrogen is mixed with the air which filled the

flask. After the air is displaced, the hydrogen, dried by passing through a tube containing calcium chloride, is lighted as it issues from a jet. If a glass bell jar is held over the flame, its surface is at once clouded by a mist which soon collects in drops of water.

Again, if a current of dry hydrogen is led through a tube filled with copper oxide, water appears when the oxide is heated, while at the same time the black oxide is changed to red metallic copper.

These syntheses of water prove that hydrogen and oxygen are the only constituents of water.

Composition of Water by Weight. — The last experiment with copper oxide and hydrogen may be carried out in such a manner as to show the proportions by weight in which hydrogen and oxygen unite to form water.[1] It is only necessary to find the loss in weight of the copper oxide, and to collect or absorb the water which is produced and determine its weight. The weight which the copper oxide loses is the weight of the oxygen in the water collected, and the difference between this weight and that of the water is the weight of the hydrogen.

The relation of the weights of hydrogen and oxygen in the water may also be found by conducting the experiments with steam and iron or magnesium in a quantitative way.[2] The oxygen is fixed by the metal, and the hydrogen with which it was combined is given off as gas. The increase in the weight of the iron or magnesium is the weight of the oxygen, and the weight of the hydrogen is found by measuring the gas, calculating its normal value, and multiplying this volume in

[1] "Quantitative Experiments," page 43. [2] *Ibid.*, page 41.

cubic centimeters by the known weight of one cubic centimeter under normal conditions. (This is a common way of finding the weight of a gas, as gases can be measured much more easily and accurately than they can be weighed.)

Careful experiments of the kind described will show that water contains very nearly eight parts of oxygen to one of hydrogen.

Composition of Water by Volume. — The relation of the volumes of oxygen and hydrogen which combine to form water can be readily calculated from the weight relations and the densities of the gases. Oxygen is almost exactly sixteen times as heavy as an equal volume of hydrogen. Hence, from the proportions by weight of eight to one, it follows that the proportions by volume must be one volume of oxygen to two volumes of hydrogen. This we find to be the case when mixtures of oxygen and hydrogen are confined over mercury and caused to unite by an electric spark. The steam produced condenses at once to water, and the volume of the water is so small that it may be left out of consideration. When the gases are mixed in the proportions given above, both disappear completely; otherwise the excess of one or the other will remain. If the experiment is conducted at a high enough temperature to keep the water in a state of gas (steam), it will be found that the volume of the steam is equal to that of the hydrogen which has entered into combination, or is equal to two thirds of the volume of both gases when they are mixed in the right proportion; that is, two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam.

When an electric current is caused to pass through dilute solutions of sulphuric acid or of sodium hydroxide, hydrogen is given off at the negative electrode and oxygen at the positive electrode. If these gases are collected separately, their volumes are found to be in the ratio of two of hydrogen to one of oxygen. This experiment is often used as a demonstration of the volumetric composition of water. It cannot, however, be carried out with pure water, as this is not acted on by the electric current; and the presence of the substances in solution obscures the interpretation of the result. It can be shown, nevertheless, that the amount of sulphuric acid or of sodium hydroxide remains unchanged, and that water alone disappears during electrolysis, so that the volumetric relation of the gases must be that in which they are combined in water. The subject of electrolysis and the function of the dissolved substances will be discussed farther on (p. 162).

CHAPTER V

LAWS OF CHEMICAL COMBINATION AND THE
ATOMIC THEORY

THE simple relation which we have found to exist between the volumes of hydrogen and oxygen in their combination with each other holds good in the reactions of other gases. It has been found that: *Whenever gases unite and whenever gases are the product of the reaction, the proportions by volume of all the gases concerned can be represented by small whole numbers.* This is called **Gay-Lussac's Law** of combining volumes.

The Hypothesis of Avogadro. — In explanation of the simple volumetric relations which are expressed in Gay-Lussac's law, Avogadro, in 1811, offered the hypothesis that: *In equal volumes of all gases, at the same temperature and pressure, there is the same number of particles or molecules.* This hypothesis has been abundantly confirmed by many facts, and is also, as we have seen, a deduction from the kinetic-molecular theory of gases (p. 27), so that it may be regarded as well established. We shall find that this hypothesis is of very great importance in our study of chemistry.

As molecules are the smallest possible particles of a substance which can retain the properties of the substance, we picture all chemical reactions as taking place between the molecules. According to the hypothesis

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of Avogadro, the formation of steam from oxygen and hydrogen consists in a reaction between a certain number of oxygen molecules and twice that number of hydrogen molecules, with the production of a number of steam molecules equal to that of the hydrogen, — each individual molecule of oxygen reacting with two molecules of hydrogen and forming two molecules of steam.

Relative Weights of Molecules. — Since we know the relations by weight as well as by volume in which oxygen and hydrogen unite, and also that the weight of the steam produced is equal to the sum of their weights (law of conservation of mass), we may find the relative weights of the molecules of hydrogen, oxygen, and steam as follows: one part by weight of hydrogen, occupying two volumes, combines with eight parts of oxygen, occupying one volume, to form nine parts of steam, occupying two volumes; as equal volumes of the gases contain equal numbers of molecules, it is evident that the molecule of steam must weigh nine times as much as the molecule of hydrogen, and that the oxygen molecule weighs sixteen times as much.

In general, *the relative weights of the molecules of different gases are the same as the relative weights of equal volumes of the gases* when determined under the same conditions of temperature and pressure; that is, as the densities or specific gravities of the gases. This applies not only to substances which are gases at ordinary temperatures, but also to all those which, like water, can be changed into gases or vapors by heat. The determination of relative molecular weights in this way is the ,most important application of the hypothesis of Avogadro.

Each molecule of water or of steam contains eight parts of oxygen by weight and one part of hydrogen; and in each molecule of every compound, the law of definite proportions of the elements (p. 7) which applies to weighable quantities must hold good.   In many instances, two or more compounds of the same elements are known, and it is found that, in such cases: *The weights of one element which combine with a given weight of another always bear a definite, fixed ratio to each other.* This is the **law of multiple proportions.**   For example : oxygen and hydrogen not only combine in the proportion of eight to one to form water, but also unite to form another compound, hydrogen peroxide, in which the proportion of oxygen is twice as great, — sixteen to one; and oxygen and sulphur form two compounds in which the weights of oxygen combined with the same weight of sulphur are as two to three.

It is also true : *That if the weights of the elements which combine with a given weight of some one element or which displace it in a compound* (as sodium or magnesium displace hydrogen in water) *are determined, all chemical combinations of these elements are found to take place between quantities which are proportional to these weights or to simple multiples of them.*   This is the **law of equivalents.** For instance, 12.16 parts by weight of magnesium, 27.9 parts of iron, 31.8 parts of copper, 3 parts of carbon, 8 parts of sulphur, and 1 part of hydrogen, each combine with 8 parts of oxygen; and we find that 12.16 parts of magnesium displace 1 part of hydrogen from water, and 31.8 parts of copper from solutions of its compounds; that 27.9 parts of iron, 31.8 parts of copper, 3 parts of carbon, and 1 part of hydrogen, each combine

with 16 (8×2) parts of sulphur; and that 3 parts of carbon combine with 1 part of hydrogen.

From such experimental facts as these a table of "combining weights" or **equivalents** of the elements can be made.

TABLE OF SOME EQUIVALENTS

Oxygen	8.	Iron	27.92
Aluminium	9.03	Magnesium	12.16
Calcium	20.045	Mercury	100
Carbon	3	Mercury	200
Chlorine	35.46	Silver	107.88
Copper	31.785	Sodium	23
Copper	63.57	Sulphur	8.017
Hydrogen	1.008	Sulphur	16.035
Iron	18.62	Zinc	32.685

As the values of the equivalents are wholly relative, showing only the ratios of the weights of the elements which combine with each other or are chemically equivalent, any value for any element could be arbitrarily chosen as the standard. As hydrogen is the lightest of the elements and has the smallest equivalent, it would seem to be the natural unit of the equivalents, and was so used for a long time. In recent years, however, oxygen with the value of 8 is employed as the standard of chemical equivalents.

A number of the elements have more than one equivalent in the different compounds which they form. In the short table just given copper, iron, mercury, and sulphur have two equivalents each. The difficulties and confusion which this leads to are avoided by the use of a single proportional weight for each element, which is called its atomic weight. The atomic weights are

based on the experimental equivalents, and are either the same as these equivalents or simple multiples of them.

The Atomic Theory. — The facts in regard to the chemical combination of the elements which we have been considering, and which are expressed in the laws of definite, multiple, and equivalent proportions, are all satisfactorily explained by the atomic theory, which was proposed by Dalton more than a hundred years ago. According to this theory each elementary substance consists of ultimate particles called **atoms**. The atoms of each element are alike in weight and in other respects, while those of different elements differ in weight and in their other properties. Molecules are formed by the chemical union of atoms; if the atoms are of the same kind, the result is an elementary substance; if the atoms are of different kinds, a compound is formed. The atoms retain their weight unchanged through every transformation which may occur, and molecular weights are the sum of the weights of the atoms in the molecule. While the weights of the single atoms as well as those of the single molecules are far too small for actual weighing, figures representing their relative weights may be derived from the values of the chemical equivalents, by the aid of determinations of the molecular weights of their compounds and of other considerations.

The atomic and molecular theories have been and are of the greatest service to chemistry. They aid the imagination in its attempt to gain a concrete picture of matters far beyond the reach of sight or touch, they correlate the facts which have been accumulated by experiment, and they have fulfilled in a high degree that

function of a theory which consists in suggesting new lines of successful experimental research. We must not, however, fail to remember that they are theories and not facts. This is emphasized by the failure of the atomic theory to explain the striking fact that all of the properties of an elementary substance, except its weight, disappear when it enters into combination with other elements. We should expect the atoms, even in the closest contact with each other, to retain all of their individual properties. This disappearance of the original properties, and the appearance of an entirely new set of properties, suggests a most intimate blending or interpenetration of the atoms, rather than a mere juxtaposition. The atomic theory furnishes no interpretation of this.

Recent investigations in electricity and radioactivity indicate that the atoms contain still smaller particles. Some of these particles are called corpuscles or electrons, and their mass has been reckoned to be about one thousandth of that of the hydrogen atom. But these interesting theories do not disturb the validity of the atomic theory as an explanation of most of the facts of chemistry. Long experience and countless experiments have proved that, whatever the ultimate composition of the atoms, these chemical units are unchangeable within the limits of our usual operations.

Symbols and Formulas. — For convenience in expressing the composition of substances and their reactions in accordance with the atomic theory, the atoms are represented by **symbols** consisting of the initial letters of the name of the element, or of this letter with another of the name when this is necessary to avoid confusion. In some cases the symbols are taken from the Latin names;

thus, while the symbol for the oxygen atom is O, that for the copper atom is Cu (cuprum). Molecules are represented by **formulas** which contain the symbols of the constituent atoms; thus CuO is the formula for copper oxide.   Two or more atoms of the same element are indicated by coefficients or by subfigures, as $2\,O$ or O_2, CO_2; and two or more molecules, by coefficients, as $3\,CuO$, $5\,CO_2$.

Atomic Weights. — As the atomic theory is an explanation of the fixed combining proportions of the elements, it is evident that the weights of the atoms must either be those of the equivalents or else stand in some very simple relation to them.   In the case of water, the experimental fact that it consists of hydrogen and oxygen in the proportion by weight of one to eight could be explained by supposing that each molecule contains one atom of hydrogen weighing one, and one atom of oxygen weighing eight; but if there were two atoms of hydrogen weighing two and one of oxygen weighing sixteen, or one of hydrogen weighing one and two of oxygen each weighing four, the explanation would still hold. The value of the atomic weight of oxygen, that of hydrogen being one, clearly depends on the number of atoms in the molecule.   It is possible to reach a conclusion in regard to this by the following considerations.

If the solution formed by the action of sodium on water is evaporated to dryness, a solid is obtained which may be melted at a high temperature without decomposition.   On heating this solid with iron filings, we find that hydrogen is given off.   This hydrogen must have come originally from the water on which the sodium

acted, although hydrogen was also set free in this action. Further, it can be proved that the amount of hydrogen set free by the action of a given weight of sodium on water is exactly equal to that obtained from the sodium compound which results from this action.   We conclude, therefore, that the hydrogen in water is divisible into two equal parts, and that the molecule of water contains at least two atoms of hydrogen.

In a different way we may reach a conclusion in regard to the number of oxygen atoms in the water molecule. If we represent the volumetric relations of hydrogen, oxygen, and steam by the following diagram in which equal squares indicate equal volumes, and suppose that each of these volumes contains 1000 molecules of gas,

1000	1000

Hydrogen

1000

Oxygen

1000	1000
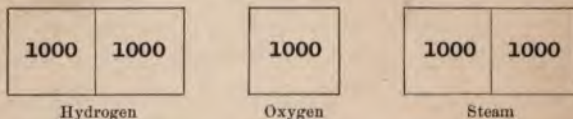
Steam

we see at once that, since each molecule of steam must contain at least one atom of oxygen, each oxygen molecule must consist of at least two atoms to supply the number necessary ; and since we have seen that there are at least two atoms of hydrogen in a molecule of steam (water), it also appears that the hydrogen molecules must consist of at least two atoms each. Since two atoms in each of the hydrogen and oxygen molecules are enough to explain the matter, and we have no reason for supposing that the molecules contain more than two, the molecules of these gases are considered to consist of two molecules each, and their formulas are H_2 and O_2, the subfigures being used in-

stead of coefficients $(2\,H, 2\,O)$, to indicate the union of the atoms in the molecules. In the same way we decide that the molecule of water contains only two atoms of hydrogen and one of oxygen, and that its formula is, therefore, H_2O.

Since two molecules of hydrogen, containing four atoms of hydrogen, unite with one molecule of oxygen, containing two atoms of oxygen, the atomic weight of oxygen is twice the number which expresses its equivalent, or sixteen times that of hydrogen. *This value for oxygen*, $O = 16$, *is the standard for all atomic weights* adopted by international agreement in place of $H = 1$, which was for many years the standard. If the ratio between the atomic weights of hydrogen and oxygen was exactly one to sixteen, this change would be of no significance; but recent very exact determinations have shown that the ratio is $1 : 15.88$, or $1.008 : 16$. The exact values for the atomic weights are, of course, based on the equivalents which are determined by careful quantitative determinations. In the case of hydrogen and oxygen, such determinations show that these elements unite to form water in the proportion of 1.008 to 8, and a double value is given to the atomic weight of oxygen for the reasons which have been discussed.

Molecular Weights. — The weight of the molecule is the sum of the weights of the atoms it contains. The molecular weight of oxygen, $32\,(2 \times 16)$, serves as the standard, and the molecular weights of hydrogen and of steam are, therefore, $2\,(2.016)$ and $18\,(18.016)$, respectively, which are in the same proportion as the relative densities of the gases. The molecular weights of all other

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gases and vapors can be determined, therefore, from their densities, by comparison with the density of oxygen or of some other gas whose molecular weight is known. The densities are either expressed as the weights of one cubic centimeter or one liter of the gas or vapor under normal conditions, or as the ratio which the weight of any volume bears to the weight of an equal volume of some other gas taken as unity (specific gravity). Thus, the weight of a normal liter of oxygen is 1.429 grams, of hydrogen, 0.090 gram, of air, 1.293. The density of oxygen with reference to air as unity is 1.105, that of hydrogen is 0.069; and the density of oxygen with reference to hydrogen as unity is 15.88, and that of air is 14.48. The figures in these different sets of values obviously stand in the same relation to each other, and either set may be made the basis for the determination of molecular weights.

In the actual determination of relative densities, air is most commonly taken as unity. Since air is a mixture of gases, we cannot properly speak of the molecular weight of air; but, for the purpose of translating densities with reference to air as unity into molecular weights, we may use the average molecular weight of the air. This is found from the density of oxygen as follows :

Density of Oxygen		Air as Unity		Mol. Wt. of Oxygen		Av. Mol. Wt. of Air
1.105	:	1.000	: :	32	:	$x = 28.96$

or

Liter of Oxygen		Liter of Air		Mol. Wt. of Oxygen		Av. Mol. Wt. of Air
1.429	:	1.293	: :	32	:	$x = 28.96$

When air is taken as unity in density determinations, molecular weights are found by this proportion:

$$1.000 \text{ (density of air)} : \text{Density of Gas} ::$$
$$28.96 : \text{Mol. Wt. of Gas};$$

or the molecular weight is equal to the density (air $= 1$) multiplied by 28.96.

Gram-Molecular Weight and Volume. — Since the molecular weights of gases are in the ratio of the weights of equal volumes, the molecular weight of any gas expressed in grams must always occupy a definite volume which will be the same in all cases. Thus, one liter of oxygen weighs 1.429 grams, and hence 32 grams of oxygen will occupy $32 \div 1.429 = 22.4$ liters; one liter of hydrogen weighs 0.09 gram, and 2 grams of hydrogen will occupy $2 \div 0.09 = 22.4$ liters. Similarly in the case of all gases and vapors, it will be found that the molecular weight in grams divided by the weight of a normal liter will give 22.4. *The molecular weight expressed in grams is the* **gram-molecular weight**; and *the volume*, 22.4 *liters*, is called the **gram-molecular volume**. These terms are conveniently shortened to **molar weight** and **molar volume**.

The molar weight of a gas or vapor, and consequently its molecular weight, may, therefore, be found by calculating from the known weight of any volume the weight of 22.4 liters. Thus, if it is found that the weight of 340 cubic centimeters of carbon dioxide, under normal conditions, is 0.668 gram, the following proportion gives the molecular weight:

$$0.340 : 22.4 :: 0.668 : x, \text{ hence } x = 44.$$

The knowledge of molecular weights is a very important means of deciding the value of atomic weights, and when the method of gas or vapor density cannot be employed (because the compound is not volatile) other ways are used, which will be referred to later.

Meaning of Formulas. — The formula of a compound represents the facts in regard to its composition, which have been obtained by analysis or synthesis, in terms of the atomic weights. If the atomic weights are known, a formula is derived from its composition by weight as follows:

It is evident that the numbers of atoms in the same weights of different elements must be in the inverse ratio of the atomic weights. If, therefore, we divide the figures which express the proportion of each element in a compound by the atomic weight of this element, the quotients will show the relative number of atoms of each element in the compound. For instance, in water we have found that the hydrogen is to the oxygen as one to eight; on dividing these figures by the atomic weights: $1 \div 1 = 1$, $8 \div 16 = 0.5$, we see that the quotients are in the ratio of $2 : 1$, and therefore the simplest formula for water is H_2O. The compound which magnesium forms with oxygen contains 60.32 per cent of magnesium and 39.68 per cent of oxygen: $60.32 \div 24.32$ (atomic weight of magnesium) $= 2.48$, and $39.68 \div 16 = 2.48$, whence the formula of the compound is MgO.

These simplest formulas obtained from the composition are called **empirical formulas**. Where it is possible to find the molecular weight by gas or vapor density determinations or by other methods, the empirical for-

mula is changed, if necessary, to agree with the molecular weight, and this final formula is called the **molecular formula.** This change involves merely the adoption of some simple multiple of the empirical formula. The density of steam leads to the molecular weight of 18 for water, as we have seen, so that the molecular formula for water is the same as its simplest formula, H_2O. In hydrogen peroxide the proportions of hydrogen and oxygen are one to sixteen, which would give the empirical formula, HO; but the molecular weight of this substance has been found to be 34, hence the molecular formula is H_2O_2.

The quantitative determinations of composition and the derivations of formulas which are described in this book are simply in illustration of methods which may be used. It must be understood that in all cases formulas are based on similar experimental evidence, and that a formula is only a compact representation of experimental facts.

Chemical Equations. — The combination of hydrogen and oxygen to form water is conveniently represented in the form of an equation whose terms are molecular formulas:

$$2\,H_2 + O_2 = 2\,H_2O.$$
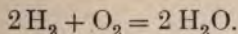
The equation shows not only what substances take part in the reaction and what the product is, but also their proportions by weight, and, when they are gases, the proportions by volume. Four parts by weight of hydrogen (2×2) and thirty-two parts of oxygen (16×2) produce thirty-six parts $(2 \times 2) + (2 \times 16)$ of water; and two molecules (volumes) of hydrogen combine

with one molecule (volume) of oxygen to form two molecules (volumes) of steam.

Similar equations may be used for all chemical reactions. A simpler form of the above equation, $2H + O = H_2O$, would give the weight relations; but when elementary gases are concerned, it is always better to use formulas which represent molecules and not single atoms, and which thus represent the relations by volume as well as by weight.

As further illustrations of equation making, we may represent some of the reactions we have studied as follows:

Steam	Magnesium	Magnesium Oxide	Hydrogen

$$H_2O + Mg = MgO + H_2.$$

Water	Sodium	Sodium Hydroxide	Hydrogen

$$2H_2O + 2Na = 2NaOH + H_2.$$

Water	Iron	Iron Oxide	Hydrogen

$$4H_2O + 3Fe = Fe_3O_4 + 4H_2.$$

Copper Oxide	Hydrogen	Copper	Water

$$CuO + H_2 = Cu + H_2O.$$
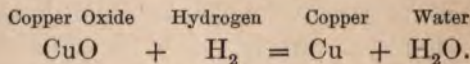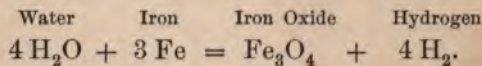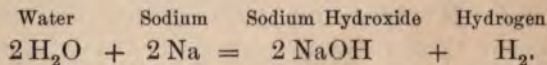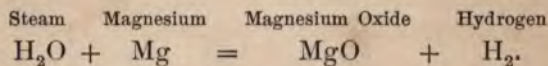
Reactions and Reagents. — The two-sidedness of most chemical changes should be always kept in mind. While in some cases decomposition of a single substance occurs, as in the evolution of oxygen from potassium chlorate, in the majority of chemical phenomena which we study, two or more different substances take part, and both are changed. We are apt to look at the result from a single point of view, — that of the change which seems most important, and disregard, more or

less completely, the other transformations. The terms
reaction and reagent, which are commonly employed,
imply the dual relation which usually exists. A **reaction** is an action of one substance upon another which
simultaneously acts on it, and each of the reacting substances is, properly speaking, a **reagent**.

Classification of Reactions. — The chief types of chemical change are classified as follows : 1. **Combination** or
synthesis, as in the union of hydrogen and oxygen to
form water. 2. **Decomposition** or **analysis,** as in the
separation of oxygen and mercury when mercuric oxide
is heated. 3. **Substitution,** as when magnesium takes
the place of hydrogen in steam. 4. **Double decomposition** or **metathesis,** where the constituents of two substances change places. We have had no illustrations of
this kind of reaction, but it may be symbolized thus:

$$AB + CD = AC + BD, \text{ or } = AD + BC.$$
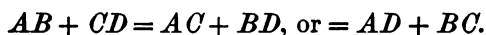
CHAPTER VI

OXYGEN AND OZONE

OXYGEN

OUR knowledge of oxygen unmixed with the other gases of the air begins with an experiment made by Joseph Priestley, in 1774, in which he obtained the gas by heating red oxide of mercury. Lavoisier soon afterwards showed that this gas was identical with the chemically active gas of the air and that it was an elementary substance. He named it oxygen (acid former) in the belief that it was an essential constituent of all acids.

Oxygen is the most abundant of the elements. In the free condition it constitutes 23 per cent of the weight of the air; and in combination it forms eight ninths of the weight of water, and about one half of the weight of the crust of the earth. It is also a constituent of most plant and animal substances and of many compounds of chemical manufacture.

Preparation. — Oxygen is obtained from air on a commercial scale by means of barium oxide. This substance combines with oxygen when heated to about 500°, and the reaction is reversed at a higher temperature. By keeping the oxide at an intermediate temperature and altering the pressure, oxygen is alternately absorbed at the higher pressure, and disengaged in a partial vacuum. The latter method is employed in the **Brin process** of

making oxygen. The oxygen is nearly pure and is sold in compressed form in steel cylinders. Oxygen is also obtained from acid or alkaline solutions by means of the electric current (electrolysis), an equivalent quantity of hydrogen being simultaneously produced ; and from a number of compounds by heating them alone or with other substances. The common method for laboratory preparation is from potassium chlorate, which gives off about 39 per cent of its weight of oxygen when heated. In practice, the chlorate is mixed with manganese dioxide, since in this case the oxygen is given off at a lower temperature and the evolution is under better control. At the end of the operation the manganese dioxide is found to be unchanged. Several other substances have the same effect in aiding the decomposition of potassium chlorate, and we shall meet with many instances where the presence of substances which appear to take no part in the chemical reaction cause it to proceed at a lower temperature or more rapidly. Such substances are called **contact agents**, or **catalyzers**, and their action is called **contact action** or **catalysis**.

Other laboratory methods for making oxygen are : the reaction of sodium peroxide and water, and the reaction of potassium permanganate with sulphuric acid. All these reactions for making oxygen will be discussed, and equations given, under the head of the compounds which are used.

Properties.— Oxygen is a colorless, odorless, and tasteless gas. It is about one tenth heavier than air, one liter under normal conditions weighing 1.429 grams. The weight of a measured volume may be determined by collecting the gas given off from a weighed amount

of potassium chlorate or mercuric oxide, and finding the loss of weight of these substances.[1]   Oxygen is slightly soluble in water, about three volumes of oxygen dissolving in one hundred volumes of water at ordinary temperatures.   The solubility of oxygen in water, even in this small proportion, is of great importance, as the life of fishes depends on its presence, and the dissolved oxygen helps to purify natural waters by destroying organic matters which they often contain.   Liquid oxygen has a pale blue color, and boils at $-182.5°$.

At ordinary temperatures the chemical action of oxygen is usually very feeble.   A few gases combine with it at once, but most substances are oxidized slowly, if at all, and generally only in the presence of moisture or carbon dioxide.   The rusting of iron and the tarnishing of some other metals, such as zinc, lead, copper, the decaying of wood, the luminosity of phosphorus, and the drying of linseed oil in paint, are instances of this slow oxidation.   At higher temperatures the action goes on rapidly, and when once started, the heat developed by it is usually sufficient to maintain it.   The temperature necessary to bring about this self-sustaining rapid oxidation is called the **kindling temperature** or the temperature of ignition.   This is very different for different substances, phosphorus igniting at $45°$, sulphur at a much higher temperature, and hydrogen at a red heat.   The amount of heat produced by the oxidation of a given weight of a substance is the same whether the action is slow or rapid; and if the heat resulting from a slow combustion is not too rapidly dissipated by conduction and radiation the temperature

[1] " Quantitative Experiments," page 28.

may rise to the kindling point. This often occurs even in the diluted oxygen of the air: A stick of phosphorus left to itself in air may finally kindle; heaps of oily rags have often been the starting point of disastrous fires. In the same way fires sometimes start in bunkers of soft coal and in heaps of other combustible materials. The rate of oxidation as well as that of all other chemical actions is greatly influenced by the extent of surface of the solid or liquid which is exposed to the action. Finely divided phosphorus left by evaporation of its solution in carbon disulphide on filter paper bursts into flame at once; iron in the form of powder is readily ignited, and when prepared under special conditions oxidizes spontaneously when brought into the air.

The most important instance of slow combustion is that which occurs in connection with respiration. The oxygen of the inspired air passes into the blood and is carried to all parts of the body, oxidizing the tissues, and the heat produced by this chemical action maintains the bodily temperature. The carbon dioxide which results from this oxidation is brought back to the lungs and exhaled into the air.

While the amount of heat produced by the oxidation of a definite weight of a given substance is always the same whatever the rate of the oxidation, the temperature depends on the rate, being higher in each case as the rapidity of the reaction is greater. Consequently, combustion in oxygen gives higher temperatures than in air, and oxygen is used for this purpose in the oxyhydrogen blowpipe. Oxygen has also found an interesting industrial application in cutting steel. When the temperature of the steel at one point has been sufficiently

raised by the oxyhydrogen blowpipe, a jet of oxygen carries on the combustion of the steel in a narrow line, so that massive blocks are quickly cut through. Pure oxygen is also used for inhalation when, through disease, the lungs fail to supply the necessary amount from the air, or when the air is impure, as in submarine boats, or too rare, as in balloon ascensions.

Oxygen combines directly with all of the non-metallic elements except those of the halogen group and the inert gases of the air; and with all of the metals with a few exceptions. Compounds with these metals and with all of the halogens except fluorine can be made indirectly. Substances which contain a single element in combination with oxygen are called **oxides**, and in general the termination " ide " is used in naming compounds of two elements, as, for instance, sulphide, carbide, hydride. Very many compounds contain oxygen combined with two or more elements, and the abundance and importance of oxygen compounds is so great that we shall constantly meet with them in our study.

Phlogiston. — For a long time in the history of chemistry so little attention was paid to the weight relations in chemical reactions that a theory prevailed to the effect that combustible substances contained something termed fire-stuff, or **phlogiston**, which was lost when the substance was burned. The oxide of a metal was considered to be the metal without its phlogiston, and the recovery of the metal by heating its oxide with carbon or hydrogen consisted in the restoration of phlogiston. The phlogiston theory was dominant for over one hundred years. It coördinated many facts, and on this account was useful, but ignored the weight

changes which accompany chemical changes and which, as we have seen, are of fundamental importance in following and interpreting chemical reactions. In 1775 Lavoisier showed by his quantitative experimental work and by his clear reasoning that loss of phlogiston was really addition of oxygen, and restoration of phlogiston, removal of oxygen, — that the hypothetical phlogiston did not exist, — and thus laid the foundation of modern chemistry.

Tests of Oxygen. — The usual test for free oxygen is the kindling of a glowing splinter of wood. Only one other gas gives this test (nitrous oxide), and we shall learn how to distinguish it from oxygen. Oxygen in compounds is detected in some cases by the evolution of the gas when they are heated, in others by recognizing some oxygen compound formed in a chemical reaction, such as water produced by the action of hydrogen.

OZONE

When electric sparks pass through air, and when phosphorus oxidizes slowly in moist air, a peculiar odor is observed, which resembles that of burning sulphur. This odor is evidence that a new gaseous substance is formed under these conditions. The same substance is produced when pure oxygen is subjected to the so-called silent electric discharge; and this fact indicates that this new substance, which is called **ozone**, consists only of oxygen. In fact, when heated to 250°, ozone is wholly changed into ordinary oxygen. It is found that the change from oxygen into ozone and that of ozone into oxygen is accompanied with a definite change in volume,

three volumes of oxygen giving two volumes of ozone, and two volumes of ozone, when heated, becoming three volumes of oxygen. A given volume of ozone weighs, therefore, half as much again as the same volume of oxygen, and hence the molecular weight of ozone must be one and a half times that of oxygen, or 48. It follows from this that the molecule of ozone contains three atoms of oxygen and has the formula O_3, while that of ordinary oxygen, as we have seen, is O_2. The change from one into the other is represented thus:

$$3\,O_2 \rightleftarrows 2\,O_3.$$
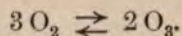
The arrows indicate the reversible character of the reaction.

Ozone can be made in several ways besides those which have been given, but in no case is it possible to convert all of the oxygen into ozone, because it is too unstable a compound and changes too readily into ordinary oxygen. Consequently, the volume relations which have been stated are derived from experiments made with mixtures of ozone and oxygen. Ozone is a gas of a faint blue color and can be condensed to a blue liquid. It is very much more soluble in water than is oxygen.

Ozone is, chemically, an active oxidizing agent. In the presence of moisture it acts on all metals, except gold and platinum, and on phosphorus, sulphur, and iodine, with the formation of oxides; and it oxidizes many inorganic and organic substances. Ozonized air containing about one per cent of ozone is employed to some extent for bleaching wax, starch, and ivory, for purifying drinking water, and for some other purposes.

Paper which has been dipped in starch paste containing a little potassium iodide is turned deep blue by ozone. This reaction may be used as a test for ozone, but only in the absence of other substances which have a similar effect.

We shall find that other elements besides oxygen can be obtained in different forms with different properties. The different forms are called **allotropic modifications.** Thus ozone is an allotropic modification of oxygen.

CHAPTER VII

HYDROGEN AND HYDROGEN DIOXIDE

HYDROGEN

WE owe our first definite knowledge of hydrogen as an independent gas to Cavendish, who obtained it by the action of acids on certain metals in 1766 and described its properties.

Hydrogen in a free state is found in the gases which escape from volcanic vents, and in certain deposits of rock salt. It is also a component of natural gas. In combination it forms one ninth of the weight of water, and is a constituent of petroleum and of all vegetable and animal substances.

Preparation. — Hydrogen may be set free from certain of its compounds by the action of metals: from water, by sodium and some other metals at ordinary temperatures, and by magnesium, iron, and other metals when heated; from hydroxides, such as sodium hydroxide, NaOH, and from dilute acids, such as sulphuric or hydrochloric acids, by the action of zinc, aluminium, etc. Hydrogen is also evolved at the negative electrode in the electrolysis of solutions of acids, alkalies, and some salts. The usual method of laboratory preparation is by the action of dilute sulphuric or hydrochloric acid on zinc.

Properties. — Pure hydrogen is a colorless, odorless,

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and tasteless gas, but as usually prepared has a dis-
agreeable odor due to traces of other gases derived from
impurities in the materials employed.   It is the lightest
substance known, being about 14.5 times lighter than air.
One liter of hydrogen under normal conditions weighs
very nearly 0.09 gram.   The boiling point of liquid
hydrogen is only 20.5° above the absolute zero.   Hy-
drogen is very slightly soluble in water.   It is absorbed
by a number of metals in considerable quantities, —
palladium under the most favorable conditions taking
up about 900 times its volume of the gas.

Hydrogen is usually collected over water, but because
of its lightness it may be collected by displacing air in
a vessel which is held mouth downward.   It may also
be poured up through air and siphoned upward.   The
diffusion of hydrogen is very rapid (p. 24).   Its rate of
diffusion as compared with air may be shown by means
of an unglazed porcelain cylinder connected with a glass
tube whose end is in water.   When a bell jar of hydro-
gen is placed over the cylinder, bubbles of air are
driven rapidly out of the cylinder and tube through the
water, because the diffusion of the hydrogen into the
cylinder is so much more rapid than the opposite
movement of the air ; and when the bell jar is removed,
water rises in the tube, because of the partial vacuum
in the cylinder which results from the rapid escape of
the hydrogen.

Chemically, hydrogen shows little activity at ordinary
temperatures, and even at high temperatures it unites
readily with only a few elements.   Its most notable
activity is exhibited towards oxygen.   It ignites in air
or in oxygen at a red heat and burns with an almost

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colorless and very hot flame. When oxygen is led into a jet of burning hydrogen, as in the oxyhydrogen blow-pipe, a temperature is produced which is high enough to melt platinum and silica, and to give an intense light when it is directed against a piece of lime, as in the Drummond or "lime light." A mixture of hydrogen and oxygen in the proportion in which these gases unite to form water explodes sharply when ignited. If mixtures of the gases are made in other proportions, it will be found that the explosions become duller as the proportion of either gas is increased, and that with a certain excess of either hydrogen or oxygen no explosion occurs. These experiments may be conveniently made by blowing soap bubbles with the mixed gases, and touching the bubbles with a flame. The excess of either gas which can take no part in the chemical action retards it by diluting the mixture. Explosions which result from chemical reaction are due to the rapidity with which the reaction takes place and are more violent as reaction is more rapid. A mixture of air and hydrogen explodes less sharply than one of oxygen and hydrogen because of the presence of nitrogen, and the most favorable mixture is that of five volumes of air and two of hydrogen.

Hydrogen can be ignited by means of finely divided platinum in the form known as platinum sponge. When the sponge is brought into a jet of hydrogen it is quickly heated to the ignition point of the hydrogen, while suffering no chemical change itself. This is another instance of contact action (p. 57).

Uses of Hydrogen. — Hydrogen is used on account of its lightness for filling balloons, and, on account of the

high temperature it gives in the oxyhydrogen blow-pipe, for working platinum and other substances which have high melting points.

Reduction. — Hydrogen not only combines with free oxygen, but can also unite with the oxygen of many compounds with the formation of water. When oxygen is withdrawn from a compound in any way, the compound is said to be reduced. Hydrogen is, therefore, a **reducing agent.** It should be noted that a reducing agent in its action is itself oxidized. Thus oxidation and reduction are seen to be terms which describe the same reaction from opposite points of view. When hydrogen acts on copper oxide (p. 38), the reaction is an oxidation from the hydrogen point of view, and a reduction from that of the copper.

Phenomena of the Nascent State. — While hydrogen gas shows marked chemical activity only when heated, reductions by hydrogen often proceed rapidly at ordinary temperatures in solutions in which the hydrogen is being generated by the action of metals on acids or alkalies, or by electrolysis. A solution of potassium permanganate, for instance, soon loses its color when sulphuric acid and zinc are added to it, while it is scarcely changed when hydrogen gas bubbles through it in the presence of zinc or of sulphuric acid alone. The usual explanation which is given for this greater activity of hydrogen is, that, when hydrogen is being set free, or is **nascent**, it is liberated in single atoms. The atoms under ordinary circumstances unite with each other to form molecules of two atoms each (H_2), but in the presence of a reducible substance find a stronger attraction to oxygen. We must suppose the

atoms in all molecules are held together by a certain amount of energy which must be overcome before they can enter into new combinations. That is, a separation of molecules into atoms must precede most chemical reactions. Atoms before their union into molecules should show, therefore, a higher activity than when combined in molecules.

Hydrogen is also made more active by the presence of certain substances. Potassium permanganate solution, in which finely divided platinum in the form of platinum black is suspended, is reduced by a current of hydrogen gas; and the hydrogen absorbed in palladium has a reducing power greater than that of free hydrogen. In both of these cases the metals suffer no change. Further, the activity of nascent hydrogen may vary with the material in contact with which it is generated; for instance, with the nature of the negative electrode used in its production by electrolysis. In these cases we may suppose the effect of contact action to modify the nascent action.

The greater chemical activity which ozone has as compared with oxygen is explained as the effect of the nascent oxygen produced in the breaking down of the molecules of ozone into oxygen:

$$O_3 = O_2 + O.$$
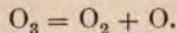
Many instances of this greater activity in the nascent state are shown by other elements.

Reversible Reactions. — Iron oxide is reduced to iron when heated in hydrogen with the formation of steam. But we have seen that iron, when heated in steam, is changed to oxide with the liberation of

hydrogen.   Here again is a reversible reaction, but one quite different from those used in making oxygen by the Brin process and ozone from oxygen.   As there are many similar reactions we will consider this one briefly.   In the first reaction the steam is swept continually from the tube containing the iron, so that the hydrogen is always in excess; in the second reaction the hydrogen escapes and the steam is in excess.   If we should inclose some iron filings and steam in a vessel and keep the temperature high enough for either reaction to go on, we should find that after a time no progress would be made in either direction; some of the iron would be oxidized, and there would be a certain proportion of hydrogen and of steam.   If some of the hydrogen could be removed, more would be formed to establish the same proportion; and if steam was allowed to escape, hydrogen would act on the oxide to restore the proportion.   The continuance of the reaction in one direction or the other depends on the relative amounts of the active substances, hydrogen and steam, or on their "concentrations."   The amounts of the solids, iron and iron oxide, present make no difference, as the smallest quantity of them produces the full effect.   The standstill of the reaction is believed not to be the result of the cessation of chemical action, but to be due to the fact that both actions are now going on at the same rate; that is, it is an instance of kinetic equilibrium.   This is a single case under a general law, called the **law of mass action** or of **molecular concentration**: *The rate of any chemical change is proportional to the active mass or molecular concentration of each of the reacting substances.*

HYDROGEN DIOXIDE

When certain oxides of metals, such as the peroxides
of sodium or barium, are treated with dilute sulphuric
or hydrochloric acids, the solution acquires marked oxi-
dizing properties. By proper treatment, a colorless,
sirupy liquid can be obtained, whose analysis and molec-
ular weight determination show that its formula is
H_2O_2. Pure hydrogen peroxide is a very unstable
compound, breaking up slowly at ordinary temperatures,
and rapidly when heated, into water and oxygen. Cer-
tain substances such as finely divided platinum act as
catalyzers in promoting the decomposition. Solutions
of hydrogen dioxide, usually containing about three per
cent of the dioxide, are widely used as a bleaching agent
for feathers, fur, silk, wool, ivory, etc., in medicine as
an antiseptic, and as a reagent in the laboratory. These
uses depend on its power as an oxidizing agent, which
is explained, as in the case of ozone, by the hypothesis
of nascent oxygen :

$$H_2O_2 = H_2O + O.$$
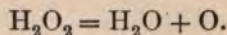
With certain compounds of oxygen, which are them-
selves somewhat unstable, hydrogen dioxide acts as
a reducing agent. Thus, potassium permanganate, in
acid solution, loses oxygen and its color when hydrogen
dioxide is added to it, the dioxide being reduced at the
same time to water. The oxygen comes off as gas.
This reaction is used to determine the oxidizing power
of hydrogen dioxide solutions, half of the oxygen which
is evolved being the effective oxygen of the dioxide.

The explanation of this mutual reduction is found in the tendency of oxygen to form molecules, O_2.

Hydrogen dioxide may be detected by the blue color which is imparted to ether when shaken with its solution after the addition of a few drops of potassium dichromate solution and sulphuric acid.

CHAPTER VIII

ENERGY

An agent which is accomplishing results of any kind is said to do **work**, and the power of doing work is called **energy**. These terms, work and energy, are used in science in very much the same sense as in ordinary conversation. A raised weight has the power of doing work, but to do this work it must fall. As it falls, the energy which it has because of its position, its **potential energy**, is lost, but energy of motion, **kinetic energy**, appears in its place. The potential energy may be restored by doing the work of raising the weight to its former position, and this work is exactly equal to the work which the weight did in its fall, such as turning the wheels of a clock or striking a blow.

There may be as many kinds of work as there are kinds of resistances to overcome : and energy appears under many different forms. Coal and the oxygen of the air possess potential energy toward each other which appears in the kinetic energy of heat when the coal is burned. This heat, transferred to steam, may be transformed into the energy of motion in the engine and the machinery which it drives. In an electric power station, this energy of motion is transformed into the kinetic energy of the electric current by means of dynamos; and the electric energy may be transformed at a distance into the energy of light and heat in lamps and

electric furnaces, or into energy of motion by means of electric motors, or into potential chemical energy as in the separation of aluminium from its oxide.

While it is found possible to convert all other forms of energy into heat, it is impossible to change the whole of a given amount of heat energy completely into an equal amount of some other kind. Further, in all transformations of the other kinds of energy, some heat is produced as the result of mechanical friction, electrical resistance, etc., so that the transformation into any desired form except heat is never quite complete.

In all transformations of energy, however, it is found that none of the energy is destroyed or lost, and that none is gained. *Energy, like matter, remains constant in amount, however its form is changed.* This statement in various forms is known as the **law of the conservation of energy.**

When we speak of the potential energy of a chemical substance, we must usually define it with reference to some other substance with which it can react. When we say that coal has a certain amount of energy, we think of its burning in air, and strictly speaking, we might just as properly discuss the potential energy of oxygen with reference to coal. It is a matter of "chemical attraction" between the coal and the oxygen, and the power of uniting and doing work is as dependent on one as on the other; just as in the case of the raised weight, the attraction of the weight for the earth is the same as the attraction of the earth for the weight.

A rather small number of chemical substances, such as ammonium dichromate or nitroglycerine, and some mixtures, such as gunpowder, form independent systems

and are capable of chemical change without the aid of other substances. The potential energy between their constituents is sufficient to carry on a reaction when it is once started.

Just as the amount of work necessary to raise the fallen weight to its former position is the same as that which the weight can do in falling, so the separation of the constituents of a chemical compound requires an outlay of the same amount of energy as that set free in their union. Hence compounds like oxides of carbon, magnesium, or phosphorus, which are formed with the evolution of a great deal of heat, are very stable compounds; while substances which require a supply of energy for their formation, such as ozone or acetylene, are unstable and liable to spontaneous decomposition with the evolution of heat. Compounds of the first class are called **exothermic** compounds and the reactions by which they are produced are called **exothermic reactions;** while the compounds and reactions of the second class are called **endothermic.**

In every chemical transformation there is an alteration in the amount of energy in the substances concerned. In exothermic reactions the available energy of the products is less than that of the substances which enter into reaction by the amount of energy liberated in the reaction; and in endothermic reactions, greater by the amount which must be supplied to produce the compounds. Heat is the form of energy which is most commonly employed to bring about chemical transformations, and is the form in which the energy set free in chemical reactions most usually appears. Electricity and light are also frequently both the cause and the product of chemical action. In

the ordinary battery, the chemical potential energy of the zinc toward the battery fluid is transformed into the energy of the electric current; and in electrolysis, the electric current is changed into chemical energy in the separated substances. Light is produced in ordinary combustions and many other chemical reactions, and often causes chemical change. It is the agent which so alters the composition and color of certain substances that photography is possible.

The energy changes in chemical reactions are usually measured in terms of heat. The **thermal unit** *is the amount of heat necessary to raise the temperature of one gram of water one degree*, and is called a **calorie**. The usual chemical equation does not indicate anything in regard to the energy changes which occur, but they may be expressed by adding to the equation the number of calories evolved or absorbed in the reaction. Thus,

$$H_2 \rightleftharpoons O = H_2O \ (+ 69,000 \text{ calories})$$
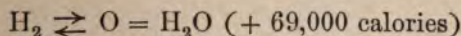
means that in the union of 2 grams of hydrogen with 16 grams of oxygen to form 18 grams of water, 69,000 units of heat are set free, and that an equal amount of energy in some form is necessary to resolve water into its elements. The decomposition of 96 grams of ozone into an equal amount of oxygen develops 61,400 calories, and therefore the formation of this amount of ozone from oxygen requires an equivalent quantity of energy:

$$3 O_2 \rightleftharpoons 2 O_3 \ (- 61, 400 \text{ calories}).$$
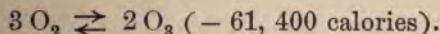
In these expressions a positive sign before the calories indicates an exothermic reaction; and a negative sign, an endothermic reaction.

In general, chemical reactions tend to proceed in such a way that energy in some form is liberated, and hence reactions which go on spontaneously when once started are exothermic reactions. The spontaneous decomposition of ozone and of hydrogen dioxide are of this character, and the energy changes which accompany them are an explanation of the oxidizing properties of these substances independent of the hypothesis of the nascent state. We may add to this hypothesis the statement that the potential energy of the elementary atom must be greater than that of the molecules, which is reasonable in the view that some energy would naturally be set free in the formation of the relatively stable molecule.

Sources of Energy. — The chief source of terrestrial energy is and always has been the sun. The heat which reaches the earth causes the winds whose power is used to drive ships and windmills ; it raises water by evaporation to the clouds, whence it falls to supply streams which furnish power for many purposes. Solar energy in the form of light and heat enables vegetation to build up its woody structure; and in prehistoric times has thus provided the material for our coal deposits, so that when we use coal to generate steam for locomotives or mills, to produce electricity by means of dynamos, or to reduce metals from their ores, we are employing solar energy, stored up ages ago.

CHAPTER IX

SULPHUR AND SULPHURIC ACID

SULPHUR has been known since ancient times, as it is found in volcanic regions in the free state. Until recently most of the world's supply of sulphur came from Sicily. The sulphur in these deposits is mixed with earthy substances and rock from which it is readily separated by taking advantage of its low melting point. Rich deposits also exist in Louisiana several hundred feet below the surface, where the sulphur has apparently been separated out of gypsum by bacterial action. The sulphur is obtained from these deposits by sinking pipes to them, melting the sulphur with superheated water, and forcing it to the surface by compressed air. A large part of the supply of sulphur now comes from this source.[1]

Sulphur occurs in large amounts in combination, especially with metals in sulphides, and with metals and oxygen in sulphates. The natural sulphide of iron, pyrites, is a well-known mineral, and a number of sulphides, such as those of lead, zinc, and copper, are important sources of the metals. Calcium sulphate in the form of gypsum is the most abundant sulphate. Sulphur is also a constituent of albumen and of many other animal and plant substances.

The crude and impure sulphur obtained by the melt-

[1] *Scientific American,* Aug. 4, 1906, page 80, and May 25, 1907, page 454.

ing-out process is purified by distilling it from iron retorts. The vapors are conducted into brick chambers, where at first they condense immediately to a fine powder which is sold as **flowers of sulphur.**   When the chambers become sufficiently heated, the sulphur vapors condense to liquid sulphur which is drawn off into moist, wooden molds, slightly conical in form, where it solidifies.   In this form it is called **roll sulphur or brimstone.**

Sulphur may also be obtained from pyrites (native iron sulphide) by heating it out of contact with air, and is recovered from some of its compounds in the operations of technical chemistry.

Properties. — Sulphur melts at 114.5° to a thin amber-colored liquid which goes through curious changes when further heated.   As the temperature is raised, the color becomes darker and the liquid flows less easily, until at about 200° it will no longer run out of the vessel; as the heating is continued, the liquid becomes thinner, but the color remains dark ; and at 450° it boils, giving a heavy reddish brown vapor.

When sulphur at about the boiling point is suddenly cooled by being poured into water, it forms an elastic mass called **plastic sulphur.** This condition is, however, not permanent ; after a time, it becomes hard and brittle, being changed into ordinary sulphur.

When melted sulphur is allowed to cool till a crust has formed on its surface, and the remaining liquid is then poured out through a hole broken in the crust, it is found that the sulphur in the vessel is crystallized in long amber-colored, transparent, elastic crystals which slowly change to opaque, brittle, ordinary sulphur.

There are, therefore, three well-defined allotropic

forms of sulphur: ordinary roll sulphur, which is often called **rhombic sulphur** from the form of its crystals, and is the only stable variety at ordinary temperatures; that which crystallizes from fusion, and which is called **monoclinic sulphur** from its crystalline form; and the plastic sulphur, which is called **amorphous sulphur**, since it is non-crystalline. The two crystalline varieties have different specific gravities and different melting points. Above 96.5°, which is below the melting point of either modification, the monoclinic variety is stable and the rhombic variety slowly changes into it; while below this temperature the rhombic sulphur is stable and the opposite change takes place. We shall find other instances of transition temperatures in the allotropic forms of other elements. Amorphous sulphur changes into rhombic sulphur very slowly under ordinary conditions, but the change is completed in a short time (an hour or so) when it is heated to 100°.

Ordinary sulphur is a pale yellow solid which is a poor conductor of heat and so brittle that, when a roll of it is held in the warm hand, sounds of internal rending are heard, and the roll may even break in pieces. It is insoluble in water, but dissolves in carbon disulphide and some other liquids. Amorphous sulphur is insoluble in carbon disulphide. Flowers of sulphur are partly insoluble and are a mixture of the rhombic and amorphous forms.

The atomic weight of sulphur is 32.07. The density of its vapor determined at different temperatures indicates that at 800° the molecular weight is 64.2, corresponding to the formula S_2, but that at lower temperatures mixtures of S_4, S_6, and S_8 are present.

Sulphur combines directly with many metals and non-metals. It burns in air or in oxygen with a pale blue flame and the production of a colorless gas of suffocating odor, which is usually accompanied with a slight smoke of flowers of sulphur.

Uses of Sulphur.—Sulphur is one of the components of black gunpowder and of mixtures used for fireworks. It is also used for vulcanizing rubber, and as the starting point for making various sulphur compounds, the most important of which is sulphuric acid.

SULPHUR DIOXIDE

The gas which is formed by burning sulphur extinguishes a candle flame and is itself incombustible. It turns moistened blue litmus paper red (**acid reaction**), an action which is directly opposite to the alkaline reaction shown by sodium hydroxide. It dissolves in water quite freely, about fifty volumes being absorbed by one volume of water at $15°$. More is dissolved at lower temperatures, and less at higher temperatures, and, on boiling, all of the gas may be expelled. The solution smells of the gas and has the same acid reaction. The gas cannot be collected over water, like oxygen and hydrogen, because of its solubility; but as it is more than twice as heavy as air, cylinders and flasks may be easily filled by displacement of air, or it may be collected over mercury. One liter is found to weigh 2.92 grams under normal conditions.[1] The gas is readily liquefied by means of a freezing mixture of ice and salt, and the liquid boils at $-8°$. At lower tempera-

[1] "Quantitative Experiments," pages 33 and 36.

tures the liquid freezes to a solid which melts at $-76°$. The liquid is a commercial article, and is a convenient source of the gas for experimental purposes.

Formula of the Gas.—The compound is evidently an oxide of sulphur. Its composition may be found by burning a known weight of sulphur in a tube in a current of air or oxygen, and causing the gas to bubble slowly through a weighed solution of sodium hydroxide. The solution absorbs the gas completely, and its increase in weight gives the weight of the sulphur oxide.[1]   In this way it is found that the oxide weighs twice as much as the sulphur from which it is produced; that is, that sulphur and oxygen combine in equal parts by weight. Since the atomic weight of sulphur is almost exactly twice that of oxygen, there must be twice as many atoms of oxygen as of sulphur in the compound (*cf.* p. 52). The empirical formula is, therefore, SO_2.   The formula S_2O_4, or any multiple of SO_2, would also express just as accurately the weight relations ; but from the density of the gas we may decide the molecular weight and hence the molecular formula (*cf.* p. 53).   Comparing the densities (weights of a liter) of this gas and of oxygen, we find that they are in the ratio of nearly two to one, from which we conclude that the molecular weight of the sulphur oxide is also twice that of oxygen.   This may be put in the form of a proportion:

| 1 L. Oxygen		1 L. Oxide		Mol. Wt. Oxygen		Mol. Wt. Oxide
1.429	:	2.92	: :	32	:	$x = 65.4$

The molecular weight of SO_2 is 64.07, while that of any other possible formula is some multiple of this; conse-

[1] *Ibid.*, page 54.

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quently the molecular formula of the compound is SO_2, and its name, **sulphur dioxide.**

It will be noticed that the molecular weight derived from the density is not exactly that obtained by adding the atomic weights. This is due to the fact that at the temperature at which the density of the gas is determined, sulphur dioxide is not far from its point of liquefaction, and hence shows a marked deviation from the gas laws (*cf.* p. 27). The exact figures for molecular weights are those furnished by the atomic weights, which rest upon careful determinations of equivalents, and the molecular weights obtained from density determinations serve only to indicate which of the possible formulas is the right one. Density determinations for this purpose need not be very accurate, since the possible molecular weights of a compound are usually widely different.

The formation of sulphur dioxide is represented by the following equation:

$$S + O_2 = SO_2.$$
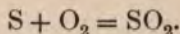
It appears from this equation that the volume of sulphur dioxide is equal to that of the oxygen required for its production. This may easily be proved to be the case by experiment.

Preparation and Uses. — Sulphur dioxide is made not only by burning sulphur, but by oxidizing pyrites and other mineral sulphides in a current of air, and enormous quantities are produced in both of these ways for the manufacture of sulphuric acid. The gas is usually prepared for laboratory purposes from sulphites or from *sulphuric* acid by reactions which will be discussed a *little farther* on.

The gas is used as a bleaching agent for silk, wool, straw, and other fibers which are injured by the use of bleaching powder, and as a disinfectant and germicide.

Chemical Behavior. — Sulphur dioxide is an active reducing agent in the presence of water. This is shown by the effect of the gas or its solution on a solution of potassium permanganate. The permanganate solution quickly becomes colorless. Since the solid permanganate loses oxygen readily when heated (p. 14), we may infer that the loss of color of its solution, in this case, as in that of the action of nascent hydrogen (p. 67), is due to a reduction. The bleaching of organic coloring matters by sulphur dioxide, which also takes place only in the presence of moisture, is in some cases the result of a reduction.

When sulphur dioxide acts as a reducing agent, it is itself oxidized (p. 67). The product of this oxidation is a substance of very great importance.

SULPHURIC ACID

If hydrogen dioxide is added to a freshly prepared solution of sulphur dioxide, the solution becomes warm, and the odor of the gas disappears. Since hydrogen dioxide is known to be an oxidizing agent, these evidences of chemical action indicate that an oxidation of the sulphur dioxide has taken place. The product of the oxidation is strongly acid and gives two distinctive tests: If part of the solution is evaporated to a small amount, and a few drops of this are brought on to a piece of paper, the moistened paper blackens when gently heated. On adding to a second portion of the solution a little barium chloride solution, a heavy white

precipitate is formed.   (Insoluble substances produced
in solutions are called **precipitates**, and the act of
their formation is called **precipitation**.)   A freshly pre-
pared solution of sulphur dioxide gives neither of these
tests (hydrogen dioxide often gives a slight cloudiness
with barium chloride).   The substance which chars
paper and forms a precipitate with barium chloride is
sulphuric acid, and may be identified with the labora-
tory reagent of this name by repeating with it these
same tests.

Sulphuric acid can also be made in a different way.
Although sulphur dioxide gas is incombustible under
usual conditions, it can be oxidized by the aid of certain
contact agents.   If a mixture of the gas with air or
oxygen is passed through a tube containing heated
platinum sponge (or fine platinum wire), a white cloud
is produced and oily drops are usually formed with
traces of moisture present in the tube.   The oily drops
char paper, and both a solution of the drops and the
water into which the cloudy product has been led give
precipitates with barium chloride.

Manufacture of Sulphuric Acid. — Both of these
methods of making sulphuric acid, — the oxidation of
sulphur dioxide in the presence of water, and the oxida-
tion of the dry gas and subsequent addition of water,
are employed in its manufacture on a large scale.   The
sulphur dioxide in both methods is obtained by burn-
ing sulphur or by oxidation of mineral sulphides, such
as pyrites, etc.

In the **lead chamber process**, the sulphur dioxide is
brought into large chambers lined with lead (to resist
the action of the acid) which are supplied with steam,

and with oxides of nitrogen (p. 138) for the oxidation.
The product, which collects on the floor of the chambers,
is a solution of sulphuric acid in water, containing 60
to 70 per cent of the pure acid. This "chamber acid"
is concentrated by evaporation in vessels of iron, glass,
or platinum; but it is impossible to drive off all the
water, because the acid begins to decompose with the
evolution of white fumes before it becomes anhydrous.

In the **contact process**, the gases from the pyrites
burners, consisting of a mixture of sulphur dioxide with
oxygen and nitrogen from the air, are led through
tubes filled with asbestos on which finely divided plati-
num has been deposited (platinized asbestos), or with
some other contact substance. Since the oxidation
product of sulphur dioxide does not dissolve readily
and completely in water, it is led into concentrated sul-
phuric acid, in which it is immediately absorbed, and
which is kept at the proper strength by a proportional
addition of water. For the success of this process it is
necessary to purify the gases by the removal of dust,
fine particles of sulphur, and especially of all arsenic
(which is usually present in pyrites), as otherwise the
contact substance soon loses its efficiency. The tem-
perature of the contact tubes must also be carefully
regulated to obtain complete oxidation of the sulphur
dioxide.

The original method of making sulphuric acid,
which was described by the alchemists, was from the
substance called green vitriol (iron sulphate). This
was roasted in the air and then heated in retorts with
the result that a fuming, oily liquid distilled, which
was known as "oil of vitriol," a name still in use for

the concentrated acid.   Later, the acid was prepared
by absorbing in water the fumes from heating a mix-
ture of sulphur and saltpeter.   This was at first done
in large glass globes, and then—in 1746—in lead-lined
chambers.   As the demand for the acid increased, the
lead chambers were made larger, and finally the process
was made a continuous one, and conducted in the way
which has been briefly described.   For over a hundred
years all the sulphuric acid was manufactured by this
process; but about 1900 the difficulties which had pre-
vented the successful operation of the contact method
were overcome,[1] and now much of the acid is made by
this process.

Properties of Sulphuric Acid. — Pure concentrated sul-
phuric acid is a colorless, oily liquid.   Its specific
gravity is 1.85.   It dissolves in water in all proportions,
and one of its most striking properties is the very con-
siderable amount of heat developed when the acid and
water are mixed.   This is so great that, in diluting the
acid, water should not be poured into the acid, but the
acid should be poured slowly and with constant stirring
into the water.   The concentrated acid removes mois-
ture very completely from an inclosed space or from a
gas which is caused to bubble through it, and is used on
this account as a valuable means for drying gases which
do not react with it.   A beaker partly filled with acid
and left standing in the air may overflow from absorp-
tion of moisture.   The concentrated acid not only takes
up water with avidity, but abstracts the elements of
water from all plant and animal tissues, destroying them
and leaving a brown or black, charred mass which is

[1] *Cf. Popular Science Monthly*, May, 1902, p. 24.

chiefly carbon. The commercial acid is often colored brown from the presence of such charred organic substances.

The strongest acid which can be obtained by evaporation or by distillation at atmospheric pressure contains about 1.5 per cent of water. When this acid is sufficiently cooled, crystals of pure, anhydrous sulphuric acid are formed, which melt at 10.5°.

Sulphuric acid acts on many metals. On some, such as copper, the action occurs only when the acid is concentrated and hot, and is attended with an evolution of sulphur dioxide; others, such as zinc, are acted on by dilute acid at room temperature with the evolution of hydrogen. In all cases crystalline solids containing the metals as constituents can be obtained from the solutions. Sulphuric acid also acts on very many compounds. On account of the great variety of chemical reactions which the acid brings about, it is of the very greatest importance in chemical operations, and we shall find it an invaluable aid in our further study. In order to understand the reactions of other substances with sulphuric acid, we must first be clear in regard to the composition of the acid and its formula.

Composition of Sulphuric Acid. — The production of sulphuric acid by the oxidation of sulphur dioxide in solution by hydrogen dioxide, and by the contact method, both show that the acid can contain no other elements than sulphur, oxygen, and hydrogen. The simplest oxidation product of sulphur dioxide, SO_2, would be a trioxide, SO_3. If we assume for the moment that the formula SO_3 represents the result of oxidizing sulphur dioxide in the contact method, sul-

phuric acid, which is formed by this trioxide with water, might be simply a solution of the trioxide in water, or a chemical compound formed with the water. In the latter case the simplest formula for the acid would be H_2SO_4.

The fact that hydrogen is evolved when dilute sulphuric acid acts on zinc shows that the acid contains hydrogen, for zinc does not act on cold water. Hence we may discard the hypothesis that the acid is a mere solution of an oxide of sulphur in water, and conclude that it is a compound of hydrogen, sulphur, and oxygen. On account of the difficulty of obtaining and dealing with the anhydrous acid, we cannot readily determine its quantitative composition by direct analysis or synthesis, as in the case of water or sulphur dioxide. Nor can its molecular weight be found from its vapor density, for it decomposes before it boils. We may, however, find its composition by weight and derive its formula, indirectly.

If the solution, in which zinc has disappeared by the action of the acid, is evaporated to dryness and gently heated until freed from water and any excess of acid, a white solid is obtained which contains the zinc as a constituent. The other possible constituents are the sulphur and oxygen from the acid. If some of the solid is dissolved in water, the solution gives a white precipitate with barium chloride, indicating that an essential part of the acid, probably all of its sulphur and oxygen, is present in the zinc compound, which thus appears to have the composition of the acid with zinc in the place of hydrogen.

The weight of the zinc compound which is formed

from 1 gram of zinc is found by experiment[1] to be 2.469 grams, and hence the weight of the sulphur and oxygen in the compound is 1.469 grams. If we assume that a molecule of the compound contains but one atomic weight of zinc, the weight of the zinc will be to the sum of the weights of the sulphur and oxygen as the atomic weight of zinc is to the sum of the atomic weights of the sulphur and oxygen, thus:

$$1.000 : 1.469 : : 65.4 : x,$$

whence $x = 96$. There are only two combinations of the atomic weights of sulphur and oxygen which will add up $96, - S_2O_2$ and SO_4. The first is thrown out of consideration because it contains a less proportion of oxygen than SO_2 from which the acid is formed by oxidation, so that the simplest formula of the compound is $ZnSO_4$.

If we determine the weight of hydrogen evolved from sulphuric acid by a given weight of zinc,[2] by measuring the volume of the gas, calculating the normal volume, and multiplying this normal volume expressed in cubic centimeters by the known weight of a normal cubic centimeter of hydrogen, we shall find that 100 parts of zinc set free 3.06 parts of hydrogen. These figures divided by the respective atomic weights will give quotients showing the relative numbers of atomic weights of hydrogen and zinc which correspond to this ratio by weight. Thus: $100 \div 65.4 = 1.53$; and $3.06 \div 1 = 3.06$. Since, $1.53 : 3.06 : : 1 : 2$, two atomic weights of hydrogen are replaced in the acid by one atomic weight of

[1] "Quantitative Experiments," page 85.   [2] *Ibid.*, pages 58 and 60.

zinc, and the formula of sulphuric acid is H_2SO_4. This formula can be verified in other ways, and corresponds with all the facts which are learned from reactions of the acid with various substances.

Reactions with Sulphuric Acid. — While dilute sulphuric acid and zinc give hydrogen gas, other products are also formed if the acid is concentrated or hot. Under these conditions gases of disagreeable odor are evolved, and the solution often becomes turbid from the separation of finely divided sulphur. This is the result of secondary reactions between "nascent hydrogen" and the acid, which contains a large proportion of oxygen, and is a somewhat unstable compound, as is shown by its decomposition by heat. The reaction with the cool, dilute acid is :

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$
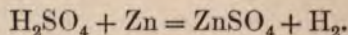
With hot and concentrated acid the following reactions with hydrogen may occur:

$$H_2SO_4 + 2\,H = 2\,H_2O + SO_2;$$
$$H_2SO_4 + 6\,H = 4\,H_2O + S;$$
$$H_2SO_4 + 8\,H = 4\,H_2O + H_2S.$$
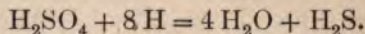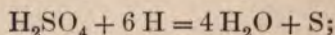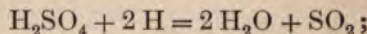
All these reactions may go on in different degrees simultaneously with the evolution of hydrogen. Consequently, when zinc and sulphuric acid are used for making hydrogen, as in the common laboratory method for preparing this gas, it is important to employ dilute acid and to keep it cool.

Another fact worthy of notice is that sulphuric acid hardly acts at all on pure zinc; but if the zinc is impure

or in contact with some metal which is not itself acted on by the dilute acid, such as platinum or copper, the reaction at once takes place. The addition of a few drops of a copper sulphate solution results in the deposition of copper on the zinc and acceleration of the action.

With metals which are attacked only by the concentrated, hot acid, such as copper, no hydrogen is evolved, but only the reduction product, sulphur dioxide:

$$2\,H_2SO_4 + Cu = CuSO_4 + 2\,H_2O + SO_2.$$
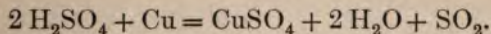
This reaction is frequently used for the preparation of sulphur dioxide. Similar reactions occur between the acid and carbon (charcoal) and with sulphur:

$$2\,H_2SO_4 + C = 2\,SO_2 + CO_2 + 2\,H_2O.$$
$$2\,H_2SO_4 + S = 3\,SO_2 + 2\,H_2O.$$
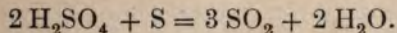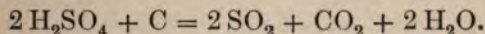
Sulphates. — The compounds which sulphuric acid forms with metals, such as $ZnSO_4$ and $CuSO_4$, are called sulphates. Most of the sulphates are stable up to a red heat, and are not changed into other salts when heated with acids, because of the non-volatility of sulphuric acid. Most of the sulphates are soluble in water, but those of calcium, strontium, and lead are very slightly soluble, and barium sulphate is practically insoluble, even in acids. This fact is used for the detection of the acid and of the sulphates. Soluble barium compounds, such as barium chloride, precipitate barium sulphate both from the acid and from solutions of sulphates, and this precipitate is not dissolved (as some other barium compounds are) by hydrochloric acid. It should be

noted that this reaction is not a test for sulphuric acid or for the individual sulphates, but for the presence of the group of elements, or **radical**, SO_4, which is their common constituent. This fact is in accordance with general experience in testing chemical compounds by precipitation, — the test does not apply to the compound as a whole, but to some element or radical which is one of its constituents. We shall discuss, further on, an hypothesis which explains this independent behavior of the constituents (p. 160).

Acids, Bases, and Salts. — Sulphuric acid is a representative of a large and important class of compounds which are called acids. **All acids** *contain hydrogen which can be replaced by metals with the production of substances which are called salts.* Most of the inorganic acids are compounds of non-metallic elements with hydrogen and oxygen. A few contain no oxygen. Soluble acids usually have an acid or sour taste, and redden blue litmus. According to the number of atomic weights of hydrogen in the molecule, which can be replaced by metals, they are termed monobasic, dibasic, etc. Sulphuric acid is a dibasic acid.

Bases *are substances which react with acids with the production of water and salts.* The inorganic bases are compounds of metals with oxygen and hydrogen in the proportion of their atomic weights. The oxygen and hydrogen are regarded as being present in the bases as hydroxyl groups or radicals, (OH). Thus, NaOH and $Zn(OH)_2$ are bases, and are called **hydroxides**. Most of these hydroxides of the metals are insoluble; but a few, such as sodium hydroxide, are soluble, and these have a caustic taste and turn red litmus blue. The
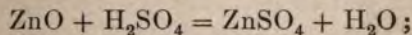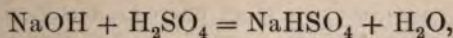
most soluble bases are called alkalies. Many oxides of the metals also react with acids with the formation of salts and water, and these, which are equivalent to the bases less the elements of water, are called **basic oxides.**
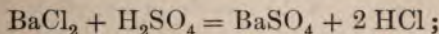
Salts are usually crystalline compounds, often containing water of crystallization, and *may be regarded as acids whose hydrogen has been wholly or partly replaced by metals.* Salts may be formed in several ways, of which the most important are these: By the action of an acid on a metal, as:
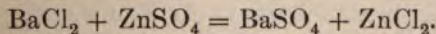
$$Zn + H_2SO_4 = ZnSO_4 + H_2;$$
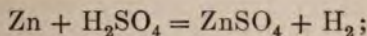
by the reaction of an acid with a base or a basic oxide, as:

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O,$$
$$ZnO + H_2SO_4 = ZnSO_4 + H_2O;$$

by the interaction of a salt and an acid, as:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2\,HCl;$$

or by the interaction of two salts, as:

$$BaCl_2 + ZnSO_4 = BaSO_4 + ZnCl_2.$$

Salts are named from the acids by changing the last syllable of the acid name. When the name of the acid ends in *-ic*, that of the salt ends in *-ate*, as in the case of sulphates. If the acid name ends in *-ous*, it becomes *-ite* in the name of the salt.

When the hydrogen of an acid is all replaced by metals, the salt is a **normal salt**; when only part of the hydrogen is replaced, as in $NaHSO_4$, it is an **acid salt**, and can enter into further reaction with bases, thus:

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O,$$
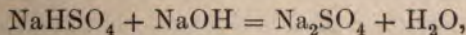
forming a normal salt. There are also **basic salts** which contain both acid radicals and the hydroxyl groups or oxygen, characteristic of the bases or basic oxides. For instance, $Pb(OH)NO_3$ is the formula of a basic nitrate of lead, derived from the base, lead hydroxide, $Pb(OH)_2$, by the replacement of one of its hydroxyl groups by the nitric acid radical NO_3. By the further action of nitric acid it would be converted into the normal lead nitrate, $Pb(NO_3)_2$.

Sulphurous Acid. — The solution of sulphur dioxide in water is believed to contain a very unstable acid whose formula is H_2SO_3, and which is named sulphurous acid, the ending *-ous* indicating, generally, a compound containing less oxygen than corresponding compounds whose names end in *-ic*. Though this acid is so easily decomposed that it can exist only in dilute solution, many comparatively stable salts are known whose composition is that of the acid, with metals in the place of its hydrogen. These salts are the **sulphites**. The sulphites are readily decomposed by acids, giving sulphurous acid, and, as this breaks down easily into water and sulphur dioxide, the sulphites are frequently used as a source of this gas:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2;$$
$$2\,NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2\,H_2O + 2\,SO_2.$$
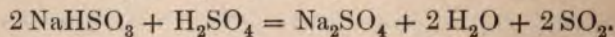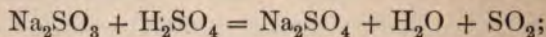
When heated, a sulphite gives the corresponding sulphate as one of the products of its decomposition. The sulphites are as readily oxidized as the sulphurous acid. In solution they are both slowly changed into sulphates or sulphuric acid by the oxygen of the air, as can be *proved* by testing, with barium chloride, solutions which

have been standing open to the air for a few hours. The solid sulphites are also gradually oxidized in the air to sulphates. Addition of very small amounts of alcohol, glycerine, or sugar restrains the oxidation of sulphurous acid and sulphites almost entirely, although the added substance undergoes no alteration. This instance of catalytic action shows that contact substances may retard as well as accelerate reactions. The bleaching action of sulphurous acid and sulphites is due to reduction of the coloring matters in some instances, in others, to the union of the sulphurous acid with them to form colorless compounds. In sunlight, these compounds are decomposed, and thus the bleaching is not permanent.

Sulphur Trioxide. — The product of the oxidation of sulphur dioxide by the aid of contact agents is sulphur trioxide, SO_3. It is a liquid which boils at 46°, and which, on cooling, gives crystals whose melting point is 14.8°. Its vapor density corresponds to the molecular weight of 80, which is that required by the formula. The liquid trioxide changes readily into a solid variety which looks like fibrous asbestos. This form has twice the molecular weight of the other, and hence its formula is $(SO_3)_2$. At about 50° it dissociates into vapors of SO_3 without melting. Sulphur trioxide unites vigorously with water and chars paper, sugar, etc., like concentrated sulphuric acid. It also unites directly with oxides of metals with the production of sulphates:

$$ZnO + SO_3 = ZnSO_4.$$
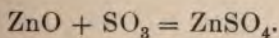
Sulphur trioxide dissolves freely in concentrated sulphuric acid, forming a fuming liquid from which crystals

of **pyrosulphuric acid**, $H_2S_2O_7$, can be obtained. Commercial **fuming sulphuric acid** consists of sulphuric acid containing varying amounts of the trioxide. It is used as a stronger sulphuric acid in certain industrial operations, and from it the trioxide may be conveniently prepared by heating.

Acid Anhydrides. — Oxides which are related to acids as sulphur trioxide is to sulphuric acid, differing from the acid by the absence of the elements of water, are called **anhydrides**. Thus, sulphur trioxide is **sulphuric anhydride**, and sulphur dioxide is **sulphurous anhydride**.

OTHER ACIDS OF SULPHUR

Eight or nine other acids are known which contain sulphur, oxygen, and hydrogen. They are all unstable compounds, and only one of the salts derived from them is of especial importance. This is the **sodium thiosulphate**, $Na_2S_2O_3$ (thio = sulphur), whose solution is the fixing bath used in photography. When a solution of sodium sulphite is boiled with sulphur, the sulphur dissolves and the thiosulphate is formed:

$$Na_2SO_3 + S = Na_2S_2O_3.$$
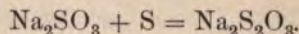
With acids the thiosulphates give thiosulphuric acid, $H_2S_2O_3$, but this at one breaks up into sulphurous acid with precipitation of sulphur:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3;$$
$$H_2S_2O_3 = H_2SO_3 + S = H_2O + SO_2 + S.$$
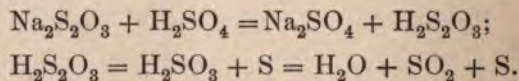
This reaction distinguishes the thiosulphates from the *sulphites*, which give no sulphur.

CHAPTER X

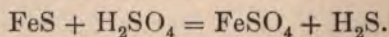## HYDROGEN SULPHIDE. VALENCE

HYDROGEN SULPHIDE

Sulphur and hydrogen do not enter readily into direct combination, though a small amount of a compound of the two elements is formed when hydrogen is led through boiling sulphur. A compound of the two is, however, readily obtained in an indirect manner by the action of acids on certain sulphides of metals. A sulphide of iron is easily made by heating a mixture of iron filings and sulphur, and when this is treated with dilute sulphuric acid, a gas of very disagreeable odor is disengaged, which burns with the odor of sulphur dioxide.

Composition of the Gas. — If a porcelain dish or a flask of water is brought into a jet of the burning gas, sulphur and moisture are deposited, showing that sulphur and hydrogen are constituents of the gas. A quantitative analysis of the pure gas may be made by leading it through a tube containing a weighed amount of copper;[1] the copper unites with sulphur, and the hydrogen is collected and its weight determined. The experiment is like that for the analysis of water (p. 38). In this way it is found that the compound consists of 94.09 per cent of sulphur and 5.91 per cent of hydrogen, and is a **hydrogen sulphide.** These figures divided by the

[1] "Quantitative Experiments," page 53.

respective atomic weights give 2.93 and 5.86, which are in the ratio of $1:2$. Hence the empirical formula of the substance is H_2S. A determination of the density of the gas [1] shows that this is also the molecular formula; for the density is found to be 1.189 (air $= 1$), and this multiplied by 28.96 (p. 51) gives 34.4, corresponding very nearly to the formula H_2S.

In order to write an equation which shall express the facts of the reaction by which hydrogen sulphide is produced from sulphuric acid and iron sulphide, we must know the formula of the iron sulphide, and also of any other products which are formed in the reaction. On making a synthesis of iron sulphide by heating a weighed amount of pure iron powder with sulphur in a covered crucible,[2] we find that it contains 63.52 per cent of iron and 36.48 per cent of sulphur. On dividing these figures by the atomic weights (Fe $= 55.85$) both quotients are found to be the same, 1.14, and, therefore, the formula is FeS. From the solution which results from the reaction with sulphuric acid a green salt may be crystallized, which is the only product besides hydrogen sulphide. This salt is in every respect like the substance formed by the action of dilute sulphuric acid on iron, and must be iron sulphate. A determination of the amount of hydrogen set free from an acid by a known weight of iron [3] shows that, as in the case of zinc (p. 89), one atomic weight of iron replaces two atomic weights of hydrogen in the acid, and therefore the formula of iron sulphate is $FeSO_4$. These facts are represented in the equation:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

[1] "Quantitative Experiments," page 36.   [2] *Ibid.*, page 69.
[3] *Ibid.*, page 60.

Hydrogen sulphide, or "sulphuretted hydrogen," occurs in volcanic gases and is dissolved in the water of sulphur springs.   It is one of the products of the decomposition of sulphur-containing organic matter, such as that of the egg.   It is formed when certain sulphides of metals are heated in a current of hydrogen, and in some other reactions ; but is usually prepared by the action of dilute sulphuric or hydrochloric acid on iron sulphide.   Since commercial iron sulphide usually contains some free iron, the gas obtained from it is a mixture of hydrogen sulphide and hydrogen.   The pure gas is prepared by the use of a pure sulphide of antimony and concentrated hydrochloric acid (p. 231).

Properties. — Hydrogen sulphide is a colorless gas of distinctive odor, and is poisonous.   Cold water dissolves three or four times its volume of the gas ; but all of the gas is driven off on boiling the solution.   On account of its solubility, the gas is usually collected for experiments by displacement of air.

Hydrogen sulphide precipitates many metals as sulphides from solutions of their salts.   Some of the metals are precipitated only from neutral or alkaline solutions, while others are precipitated even from acid solutions.   These facts are used for the separation of the metals into groups for the purpose of analyzing mixtures.   Some of the sulphides have characteristic colors which aid in identifying the metals.   Hydrogen sulphide acts directly on silver with the formation of a dark film of silver sulphide ; and the tarnishing of silverware is usually due to the presence of traces of this gas in the air.

Hydrogen sulphide is not a very stable compound.

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It decomposes easily when heated, and in solution, when exposed to the light, it is oxidized by the dissolved oxygen of the air with the formation of water and separation of sulphur. It decolorizes a solution of potassium permanganate, reduces sulphuric acid to sulphurous acid : $H_2SO_4 + H_2S = H_2O + H_2SO_3 + S$, and acts generally as a reducing agent on account of the readiness with which it dissociates into hydrogen and sulphur. The gas reacts with sulphur dioxide in the presence of moisture with the separation of all of the sulphur :

$$2 H_2S + SO_2 = 2 H_2O + 3 S.$$

This reaction is of especial interest because the native sulphur of volcanic regions has probably been deposited in this way from the volcanic gases. Sulphur is also separated from the burning gas when a cold object is brought in contact with the flame, or when the supply of oxygen is insufficient for complete combustion: $2 H_2S + O_2 = 2 H_2O + 2 S$.

The solution of hydrogen sulphide is feebly acid, and its hydrogen, like the hydrogen of acids, is replaceable by metals ; but it is not usually classed with the acids, as the sulphides can hardly be classed with the salts.

Hydrogen sulphide is recognized by its odor, and traces are detected by the darkening of a piece of filter paper which has been moistened with a solution of a lead salt, — usually the acetate.

Detection of Sulphur. — The presence of sulphur in substances may be known by the production of sulphur dioxide, hydrogen sulphide, or sulphuric acid from them. A delicate test for sulphur in solid compounds

is based on the formation of silver sulphide when silver
is brought in contact with a soluble sulphide.   The sub-
stance is fused with sodium carbonate on charcoal by
means of the blowpipe, and the resulting mass is crushed
on a silver coin with a drop of water.   If sulphur was
present, sodium sulphide is formed in the fusion, and
produces a brown stain on the silver.   The fusion is best
made with an alcohol flame, as illuminating gas usually
contains traces of sulphur compounds which would give
the test.

VALENCE

In the formulas of the compounds we have studied,
we notice that the atoms are combined in different
numbers.   Taking some of the binary compounds, we
have the formulas: H_2O, H_2S, FeS, SO_2, SO_3.   One
atom of oxygen holds two atoms of hydrogen in com-
bination; one atom of sulphur combines with two
atoms of hydrogen, one atom of iron, and either two or
three atoms of oxygen.   This varying numerical prop-
erty of the atoms is called **valence**.   Hydrogen has
this property in the lowest degree, and its valence, and
that of some other elements which resemble it in this
respect, is taken as unity in the scale of valence.   Oxy-
gen, since it can hold two atoms of hydrogen, has a va-
lence of two; sulphur in H_2S has two valences; in
FeS, since the iron atom is replaced by two hydrogen
atoms in making H_2S, both iron and sulphur have va-
lences of two; while in SO_2 and SO_3, the sulphur atom
has two and three times the valence of oxygen, or the
valence of four in SO_2, and of six in SO_3.

The valence of an element is often described by call-

ing it a **monad, dyad, triad, tetrad, pentad,** etc.   The corresponding adjectives are : **mono-, di-, tri-, tetra-, pentavalent.**

While the valence of hydrogen, and that of oxygen and some other elements, is always the same, many elements show different valences under different conditions.   This is the case with sulphur, which is a dyad towards hydrogen and iron, and acts both as a tetrad and a hexad towards oxygen.

Recalling the use of the term **equivalent** (p. 44), as the weight of an element which combines with or displaces eight parts of oxygen or the equivalent weight of some other element, *we may define the* **valence** *of an element as the number of its equivalent weights contained in its atomic weight.*   The application of this definition leads to the following rule for finding valence in the case of binary compounds :   *Find the equivalent of the element in the particular compound, and divide the atomic weight by this equivalent.*   Thus in H_2O, one part of hydrogen is in combination with eight parts of oxygen ; and the atomic weight of hydrogen, 1, divided by its equivalent, gives the valence of hydrogen, one.   In H_2S, the equivalent of sulphur (to hydrogen $= 1$) is 16 ; hence the valence of sulphur in H_2S is $32 \div 16 =$ two. In SO_2, eight parts of sulphur are combined with eight parts of oxygen ; the equivalent of sulphur here is 8, and its valence is $32 \div 8 =$ four.

Valence is sometimes represented in connection with the symbols, thus: H^I, O^{II}, S^{IV}.   In writing formulas, valences are often indicated by short lines, as in the following : $H-O-H$, $Fe=S$, $O=S=O$ or $S\!\!\begin{array}{c}\nearrow O\\[-2pt]\searrow O\end{array}$, and

$S{=}O$ (with $\nearrow O$ above and $\searrow O$ below). The number of lines from each symbol repre-
sents the valence of the element for which the symbol
stands.   Such formulas are called **graphic** or **structural**
formulas.   They represent merely the valence relations
and do not at all indicate any hypothesis as to the
arrangement of the atoms in space.

The idea of valence is extended to groups of elements
or radicals which are transferred as a whole in chemical
reactions.   Thus the hydroxyl group OH is a mono-
valent group, and the sulphuric acid radical SO_4 is
bivalent.   No element has a valence greater than eight.

So far we have considered only binary compounds.
How are the valences distributed in the formula for
sulphuric acid, H_2SO_4?   If both the hydrogen and the
oxygen were here directly connected with the sulphur,
its valence would be ten.   But two atomic weights each
of hydrogen and oxygen can be replaced by two atomic
weights of the monad chlorine, and this indicates that
the hydrogen is in hydroxyl groups, so that we write
the formula $(HO)_2SO_2$ or $\begin{array}{c} H-O \\ H-O \end{array} S \begin{array}{c} O \\ O \end{array}$, in which the
sulphur is a hexad.   The formula for iron sulphate
$FeSO_4$ becomes $Fe \begin{array}{c} O \\ O \end{array} S \begin{array}{c} O \\ O \end{array}$; and the bivalent SO_4 radi-
cal is $\begin{array}{c} -O \\ -O \end{array} S \begin{array}{c} O \\ O \end{array}$.
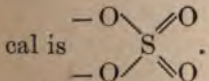
A convenient and more compact mode of expressing
the relations of the elements in complex compounds, or
the **constitution** of the compounds, is that of separating

the symbols in groups.   Thus sulphuric acid is written H_2SO_4 or $H_2.SO_4$ to indicate the acid character and the presence of the SO_4 group and replaceable hydrogen, or $(HO)_2SO_4$, to emphasize the presence of hydroxyl groups.   Similarly, the formula for thiosulphuric acid may be written $(HO)(HS)SO_2$.

An exception to the rule for finding valence in binary compounds appears in the case of hydrogen dioxide, H_2O_2.   Here 0.5 part of hydrogen is combined with 8 parts of oxygen, and by the rule, the valence of hydrogen should be two, or that of oxygen, one.   It is, however, simpler to regard the hydrogen and oxygen as having their usual valences of one and two, and, in absence of conclusive reasons to the contrary, to write the formula for hydrogen dioxide, $H-O-O-H$.   Sim-ilarly, the graphic formula for ozone is written,

Some other exceptions to the rule for finding valence in binary compounds are met with in inorganic chemistry.

CHAPTER XI

CHLORINE AND HYDROGEN CHLORIDE

COMPOSITION OF COMMON SALT AND OF HYDROGEN CHLORIDE

COMMON salt, when heated, melts at a high temperature, volatilizes somewhat, but does not decompose. It imparts to the flame of a Bunsen burner an intense yellow color like that of burning sodium, and when the flame is observed through a spectroscope, a single yellow line is seen, which is identical with that which sodium gives. We may, therefore, infer that common salt contains sodium as one of its constituents.

When salt is treated with strong sulphuric acid, a pungent gas is evolved, which fumes in air, and reddens litmus paper. Collected by downward displacement, it puts out the flame of a candle; led into water, it dissolves very freely, forming a strongly acid solution.

If the residue from the reaction of the salt and sulphuric acid is dissolved in water, a crystalline salt may be obtained by evaporation, which can be proved by the flame coloration and the barium chloride test to be sodium sulphate. We may infer from these experiments that the hydrogen of the sulphuric acid has united with the element or group of elements which was in combination with sodium in common salt, to form the gas which comes from the reaction. If we represent the

unknown part of the salt by x, we may record our inferences in the following equation, remembering that sodium is a monovalent element:

$$2\,\mathrm{Na}x + \mathrm{H_2SO_4} = \mathrm{Na_2SO_4} + 2\,\mathrm{H}x.$$
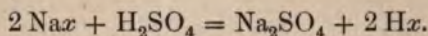
The presence of hydrogen in the gas is readily confirmed; for both it and its solution act on magnesium or zinc with the evolution of hydrogen. The next step is to attempt to separate the hydrogen from the "x." The use of an oxidizing agent naturally suggests itself; and we find, in fact, that, if the gas Hx is led through a tube in which manganese dioxide (p. 14) is heated, water is formed, and a new gas is produced, which has a greenish yellow color, an odor quite unlike that of any gas we have studied, and which bleaches moistened litmus paper. The same gas is formed when a strong solution of the acid gas Hx is gently heated with manganese dioxide or with potassium permanganate (p. 14), and may be conveniently prepared in this way for experimental purposes. It is the elementary substance **chlorine**. The gas Hx is, therefore, a compound of chlorine and hydrogen, **hydrogen chloride**, and common salt contains sodium and chlorine. That these are the sole constituents of these substances is proved by synthesis. Hydrogen and chlorine unite to form the acid gas, and common salt can be made by the direct action of chlorine on sodium.

Formula of Hydrogen Chloride. — The quantitative composition of hydrogen chloride may be found by leading the gas through a tube containing a weighed amount of iron and collecting the hydrogen which is set free.[1]

[1] " Quantitative Experiments," page 46.

The increase in the weight of the iron is due to the chlorine which combines with it, and the weight of the hydrogen, which is separated from this chlorine in the reaction and collected, is found as in the analysis of water (p. 38).   Such an analysis shows that hydrogen chloride contains 97.24 per cent of chlorine and 2.76 per cent of hydrogen.   On dividing these percentages by the respective atomic weights (35.46 and 1.008), we get the same quotient, 2.74, which shows that the formula of the gas is HCl or some multiple of this.   To decide which is the molecular formula, the density of the gas is determined.[1]   It is found that the density is 1.27 (air $= 1$), or that one liter weighs 1.64 grams.   The molecular weight is, therefore, $1.27 \times 28.96 = 36.78$; or by comparison of the weight of a liter with that of a liter of oxygen: $1.429 : 1.64 : : 32 :$ mol. wt. $= 36.7$. This molecular weight agrees nearly with that of the formula HCl, which is 36.468, and establishes this as the molecular formula for hydrogen chloride.   Since sodium is a monad, the formula for salt is NaCl.

If we now rewrite the equation for making hydrogen chloride, using these formulas, we have:

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl;$$
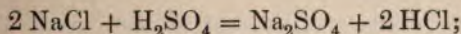
and the equation for making chlorine may be written:

$$2\,HCl + O = H_2O + Cl_2.$$
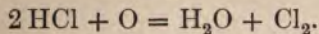
By the synthesis of hydrogen chloride from hydrogen and chlorine, and by a volumetric analysis of hydrogen chloride,[2] it is found that hydrogen and chlorine combine in equal volumes, and that the volume of the hydro-

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[1] *Ibid.*, page 35.   [2] *Ibid.*, page 47.

gen chloride is the same as the sum of the volumes of these gases. If we represent these facts in the same manner that the union of hydrogen and oxygen to form steam was represented (p. 48):

1000	$+$	1000	$=$	1000	1000
Hydrogen		Chlorine		Hydrogen Chloride	
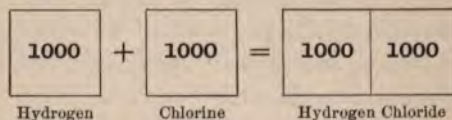
we see that the molecules of hydrogen and chlorine must consist of at least two atoms each, and write the equation representing the synthesis:

$$H_2 + Cl_2 = 2\,HCl.$$
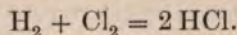
The molecular weight of chlorine is, therefore, twice its atomic weight, as in the case of oxygen and hydrogen, and this is also proved by its relative density.

Hydrogen Chloride and Hydrochloric Acid. — Hydrogen chloride is made for laboratory purposes by the action of strong sulphuric acid on common salt, or by gently heating a strong solution of the gas. It dissolves in water so freely that it must be collected by downward displacement of air, or over mercury. It acts on sodium at ordinary temperatures, and on iron and some other metals when they are heated, with the liberation of hydrogen and the formation of chlorides of the metals:

$$2\,HCl + Fe = FeCl_2 + H_2.$$
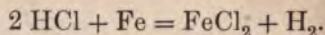
With oxides and hydroxides of the metals it gives the chlorides and water:

$$CaO + 2\,HCl = CaCl_2 + H_2O;$$
$$NaOH + HCl = NaCl + H_2O.$$
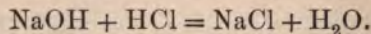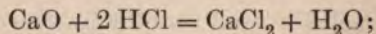
The attraction between the gas and water is so great that the gas fumes in moist air. It condenses the moisture and dissolves in it, forming an acid mist. About 450 volumes of hydrogen chloride dissolve in one volume of water at room temperature. The solution is known as **hydrochloric acid**, and also, from old usage, is called commercially "muriatic acid," a name which recalls its production from sea salt. Hydrogen chloride is often called hydrochloric acid gas, but the former name is preferable on ground of conciseness.

The strongest hydrochloric acid contains about 40 per cent of hydrogen chloride. All of the gas cannot be driven off by heating, as in the case of sulphurous acid, and when the solution reaches a strength of about 20 per cent, it distils unchanged at 110°. An acid of the same strength is finally obtained when a weaker solution is distilled. Both the composition of this acid and its boiling point vary with changes in pressure, however, and therefore it is not a definite chemical compound.

Hydrochloric acid is a strong acid and reacts with metals and their compounds in the same way as hydrogen chloride. The chlorides are mostly soluble in water, but a few are practically insoluble. Among these is silver chloride, AgCl, whose insolubility in water and in nitric acid is made the basis for the usual test for chlorine in the soluble chlorides. Silver nitrate precipitates it as a heavy white substance, which darkens on exposure to light, and is soluble in ammonia. All soluble chlorides respond to this test, as all soluble sulphates do to the barium chloride test, showing that the test concerns only the chlorine, which is their common constituent.

Hydrochloric acid is made in very large quantities from common salt and sulphuric acid, and much of it is used in making chlorine for the manufacture of bleaching powder (p. 287).

CHLORINE

Chlorine was discovered in 1774 by Scheele, who obtained it by the action of hydrochloric acid on manganese dioxide. It was called by him and other believers in the phlogiston theory, "dephlogisticated muriatic acid"; the antiphlogistonists named it oxymuriatic acid, considering it a compound of oxygen with an unknown element, "murium." Its elementary nature was long in doubt, but was finally established by Davy in 1810, who gave it its present name from the Greek, meaning greenish yellow.

Preparation. — Chlorine is usually prepared in the laboratory by gently heating manganese dioxide with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid:

$$4\,HCl + MnO_2 = MnCl_2 + 2\,H_2O + Cl_2;$$
$$2\,NaCl + MnO_2 + 2\,H_2SO_4$$
$$= Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2.$$
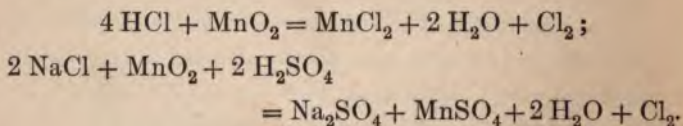
In the first reaction only half of the chlorine in the hydrochloric acid is set free; in the second all of the chlorine of the salt is obtained.

Other oxidizing agents may be used, such as potassium permanganate or dichromate; and the gas may be also made by the action of an acid on bleaching powder. When a mixture of hydrogen chloride and air is led

over heated bricks which have been moistened with a solution of copper chloride, a mixture of chlorine, steam, and nitrogen (from the air) is produced, the copper chloride acting as a contact substance. This method, known as **Deacon's process**, has been used on a large scale in making the chlorine employed in manufacturing bleaching powder. Large amounts of chlorine are also made by the use of the electric current through electrolysis of solutions of chlorides, usually of common salt.

Properties. — The greenish yellow gas has a most disagreeable and choking odor, but when small quantities of the gas are mixed with air, the odor resembles that of seaweed. Chlorine is nearly two and one half times as heavy as air,[1] and is usually collected for experiment by downward displacement of air. It dissolves in about half its volume of cold water, so that if it is to be collected over water, the water should be warm. It cannot be collected over mercury, for it combines with it. The solution of the gas, called **chlorine water**, is often used in the laboratory instead of the gas for certain reactions. When a strong solution of chlorine is cooled by ice water, crystals of chlorine hydrate are formed, which have the composition, $Cl_2, 8\,H_2O$.

Chlorine can be liquefied by a moderate pressure, and **liquid chlorine** in steel cylinders is a commercial product abroad and is now prepared in this country. The liquid chlorine is yellow, without the greenish tinge of the gas.

Chemically, chlorine is a very active substance, and combines directly with most of the elementary substances

[1] "Quantitative Experiments," page 35.

except nitrogen, oxygen, fluorine, and carbon.   The
union in many cases occurs at room temperature with
the display of great energy.   Sodium and phosphorus,
when brought into the gas, melt and ignite; antimony,
bismuth, and many other metals, when powdered or
in thin sheets, take fire with the production of their
chlorides.

A lighted jet of hydrogen burns vigorously in chlorine;
and when chlorine and hydrogen are mixed in equal
volumes, they unite explosively when ignited, or when
the mixture is exposed to the direct light of the sun or
of burning magnesium.   A lighted candle continues to
burn in chlorine, but with a dull red flame, giving off
clouds of soot; and a strip of filter paper moistened
with warm turpentine, when brought into the chlorine,
bursts into flame with the liberation of much carbon.
In these last two experiments, hydrogen chloride is pro-
duced, and they not only illustrate the great activity of
chlorine towards hydrogen, but also show that the wax
of the candle and the turpentine are compounds of
hydrogen and carbon.

Under certain conditions the action of chlorine on
hydrocarbons may be more moderate and result in a
substitution of chlorine for part or all of the hydrogen
of the compound :

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl.$$
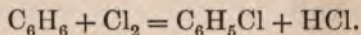
When a solution of chlorine in water is exposed to sun-
light, it slowly loses its color with evolution of oxygen,
and becomes a very dilute solution of hydrochloric acid.
In the presence of water and a substance which is readily
oxidized, chlorine effects an immediate oxidation, even

in the dark.   If it is led into sulphurous acid, for instance, this is oxidized to sulphuric acid, and hydrochloric acid is formed at the same time.   We should naturally represent these reactions as follows:

$$2\,H_2O + 2\,Cl_2 = 4\,HCl + O_2;$$
$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2\,HCl.$$
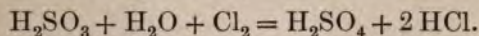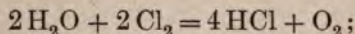
These equations express the facts which are observed. It has been found, however, that when chlorine is dissolved in water, some **hypochlorous acid**, $HClO$, is formed from the interaction of chlorine and water:

$$H_2O + Cl_2 \rightleftarrows HCl + HClO.$$
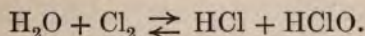
The hypochlorous acid is present in very small amount as the reaction is strongly reversible.   But it is a very unstable compound, breaking up readily into hydrogen chloride and oxygen:

$$HClO = HCl + O,$$
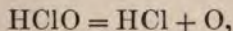
and the evolution of oxygen from chlorine water as well as the oxidizing action of chlorine in the presence of water may be explained as immediately due to hypochlorous acid.   As the hypochlorous acid present disappears, more is formed to preserve the equilibrium in the reversible reaction between chlorine and water; and finally all of the chlorine is converted into hydrochloric acid, half of it having been for an instant in the form of hypochlorous acid.   In accordance with this explanation, we should write the following equation for the reaction in the liberation of oxygen in sunlight:

$$2\,H_2O + 2\,Cl_2 = 2\,HCl + 2\,HClO = 4\,HCl + O_2.$$

I
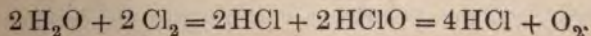
And in the oxidation of sulphurous acid:

$$H_2O + Cl_2 = HCl + HClO,$$
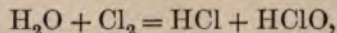
and then, $H_2SO_3 + HClO = HCl + H_2SO_4.$

In whichever manner we represent the mechanism of the reaction, the final products are the same, the energy changes are the same, and the oxidizing result is due to the action of oxygen in its active or nascent condition.

Chlorine is, therefore, an **indirect oxidizing agent in the presence of water.**

Bleaching. — The bleaching power which we noticed in the action of chlorine on litmus paper is due to such an indirect oxidation. Dry chlorine does not bleach. This may be proved by suspending a piece of dry colored cloth in a jar of dry chlorine. A piece of the same cloth in moist chlorine promptly loses its color.

Bleaching is usually carried out by "bleaching powder." This is a salt of hypochlorous acid (p. 116) and bleaches slowly in water, losing oxygen and becoming a chloride. In practice, sulphuric acid is added to the solution, and then the hypochlorous and hydrochloric acids set free react to form a solution of chlorine, containing the small amount of hypochlorous acid which can exist in such a solution, because of the slight reversibility of the reaction in the direction from right to left:

$$HCl + HClO \rightleftarrows H_2O + Cl_2.$$
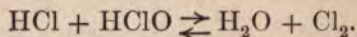
We have, therefore, the same conditions as before, a solution of chlorine in water with a little hypochlorous acid.

Most organic coloring matters are bleached by

chlorine.   Printer's ink, which owes its blackness to carbon, and most mineral colors, are not affected by it. Chlorine is not used for bleaching wool, silk, feathers, and some other substances, as these are injured by the action.   Cotton and linen, which are usually bleached with chlorine, are " rotted " by it if the action is too long continued.   To prevent this, the goods are treated with an "antichlor," when the bleaching is accomplished. The substances used for this purpose are usually the sulphite or the thiosulphate of sodium.   These salts are oxidized and the chlorine is changed into hydrochloric acid.

$$Cl_2 + H_2O + Na_2SO_3 = Na_2SO_4 + 2\,HCl.$$
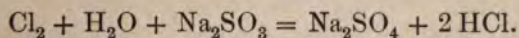
The excess of chlorine is thus immediately rendered harmless, and the hydrochloric acid and the salts formed are readily removed by washing.   On account of their oxidizing properties, chlorine and bleaching powder are largely used as disinfectants.   Chlorine is also employed as a means of extracting gold from its ores, as it unites with it directly to form soluble gold chloride, from which the gold is readily precipitated in the metallic state.

Oxides and Oxyacids of Chlorine. — Although chlorine does not unite directly with oxygen, a number of compounds of chlorine with oxygen, and with oxygen and hydrogen, can be obtained by indirect means.   They are all unstable substances, and in their decomposition can produce powerful oxidations.   The hydrogen and oxygen compounds are acids, two of which give fairly stable salts of considerable importance.   The names and formulas of these compounds are :

Chlorine monoxide, Cl_2O Hypochlorous acid, $HClO$

. . . .   Chlorous acid, $HClO_2$

Chlorine dioxide, ClO_2

. . . .   Chloric acid, $HClO_3$

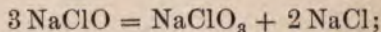Chlorine heptoxide, Cl_2O_7 Perchloric acid, $HClO_4$

Chlorous acid is the least stable of the acids, and chloric and perchloric the most stable. The salts are increasingly stable from the hypochlorites to the perchlorates. The hypochlorites and the chlorates, which are the most important salts, are made by the action of chlorine on bases. In cold dilute solutions, the hypochlorite is formed together with a chloride :

$$2\,NaOH + Cl_2 = NaClO + NaCl + H_2O.$$
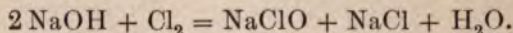
Hypochlorous acid is probably first formed and then reacts with the sodium hydroxide :

$$H_2O + Cl_2 \rightleftarrows HCl + HClO;$$
$$2\,NaOH + HCl + HClO = NaClO + NaCl + 2\,H_2O.$$
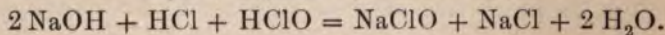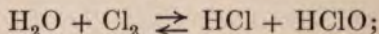
The hypochlorites when heated change into chlorates and chlorides :

$$3\,NaClO = NaClO_3 + 2\,NaCl;$$

and when chlorine is led into strong solutions of bases, the chlorates are also formed :

$$6\,NaOH + 3\,Cl_2 = NaClO_3 + 5\,NaCl + 3\,H_2O.$$
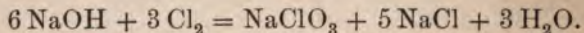
The perchlorates are formed together with chlorides and oxygen when solid chlorates are heated :

$$2\,KClO_3 = KClO_4 + KCl + O_2,$$
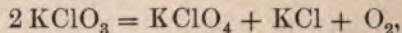
and on stronger heating break up into oxygen and chloride:

$$KClO_4 = KCl + 2\,O_2.$$
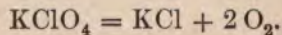
The acids may be obtained from their salts by the action of sulphuric acid. Hypochlorous acid is formed, as we have seen, in small amounts by the action of chlorine on water, and is prepared by the action of chlorine on mercuric oxide suspended in water:

$$HgO + H_2O + 2\,Cl_2 = HgCl_2 + 2\,HClO.$$
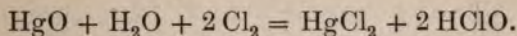
The names of the oxychlorine acids are a good illustration of the system used when more than two acids containing the same elements, but with different proportions of oxygen, are to be distinguished: **hypochlorous, chlorous, chloric,** and **perchloric.** The -*ic* acid is the most important or the most stable of the series, the -*ous* acid is that which contains the next less proportion of oxygen, while the prefix *hypo-* designates the acid with still less oxygen; and the *per . . . ic* acid is one with more oxygen than the -*ic* acid.

It should be noted that while hydrochloric acid and chlorides give a precipitate of silver chloride with silver nitrate solution, the solutions of the chlorates and perchlorates do not respond to this test. The chlorine which these salts contain must, therefore, in their solutions, be present in some combinations or radicals which form no insoluble compounds with silver.

Chlorine monoxide, Cl_2O, is a yellow gas which may be prepared by leading chlorine through a tube containing mercuric oxide, and cooled with ice water:

$$2\,HgO + 2\,Cl_2 = HgO.HgCl_2 + Cl_2O.$$
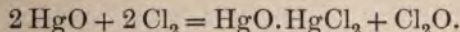
It is the anhydride of hypochlorous acid. **Chlorine dioxide,** ClO_2, is produced by the action of concentrated sulphuric acid on a chlorate, the chloric acid first formed

at once breaking up into perchloric acid, the dioxide, and water :

$$2\,KClO_3 + H_2SO_4 = K_2SO_4 + 2\,HClO_3;$$
$$\text{and},\, 3\,HClO_3 = HClO_4 + 2\,ClO_2 + H_2O.$$
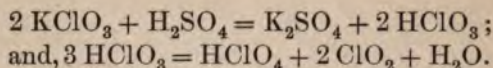
The dioxide is a heavy, dark yellow gas which has a color like chlorine and burnt sugar.   Its powerful oxidizing properties are shown by the fact that a drop of concentrated acid falling on a mixture of sugar and potassium chlorate causes ignition of the mass.   Phosphorus can be burned under water by a similar reaction. **Chlorine heptoxide,** Cl_2O_7, can be obtained as a colorless, volatile oil, by withdrawing the elements of water from perchloric acid by means of phosphorus pentoxide.   It is the anhydride of perchloric acid, as appears from the method of making it.   On contact with a flame, or on percussion, it explodes violently.

Valence of Chlorine. — Chlorine acts as a monad towards hydrogen and in most of its compounds.   In the oxides and acids and their salts, it might be regarded as a monad in such formulas as $Cl - O - Cl$, $H - O - O - O - Cl$, etc.; but compounds in which we have good reason to believe that oxygen atoms are linked together in this manner are usually unstable, and the instability would probably be greater the longer the chain of oxygen atoms.   In the case of the oxychlorine compounds, however, the stability is greater as the proportion of oxygen increases.   Hence we assume that chlorine in these acids has valences of one, three, five, and seven; with the formulas, $(HO)Cl$, $(HO)ClO$, $(HO)ClO_2$, and $(HO)ClO_3$; and that its valences in the oxides are one (Cl_2O), four (ClO_2), and seven (Cl_2O_7).

CHAPTER XII

THE HALOGEN GROUP

THREE elements, bromine, iodine, and fluorine, are closely related to chlorine in their chemical behavior and the character of their compounds. They form with chlorine a natural group which is called the halogen, or salt-forming, group, because they unite directly with metals to produce salts. None of them occur free in nature, and their compounds are not abundant.

BROMINE

When sea water has evaporated until most of the common salt has crystallized out, the last portions of solution, which are called "mother liquor," contain substances more soluble than the common salt, which yield reddish brown vapors when heated with manganese dioxide and sulphuric acid. The vapors are easily condensed to a liquid of the same color. This is the elementary substance **bromine**, the only non-metal which is liquid at ordinary temperatures. It was discovered in the mother liquor of sea water in 1826 by Balard, and occurs chiefly in combination with sodium and magnesium in connection with common salt. The principal sources from which it is obtained are the salt deposits at Stassfurt, Germany, and salt wells in Ohio and elsewhere in the United States. Bromine is pre-

pared from its salts — the bromides — either by the same method as that used for making chlorine from common salt by means of sulphuric acid and manganese dioxide :

$$2\,NaBr + MnO_2 + 2\,H_2SO_4$$
$$= Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2,$$
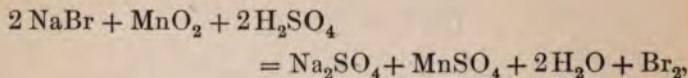
or by the displacement of bromine by chlorine :

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$
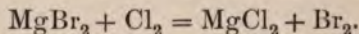
The second method is that employed at Stassfurt.

**Properties.** — Bromine is a very thin, red liquid more than three times as heavy as water. It freezes at $-7°$. It gives off vapor at room temperature and boils at $59°$. The vapor is very irritating to the eyes and throat, and the name of this element, from the Greek, indicates its very disagreeable odor. It dissolves slightly in water, imparting its color to the solution, which is known as **bromine water.** In its chemical behavior, bromine is like chlorine, entering into similar reactions and forming similar compounds. It is, however, a less active element. It bleaches as chlorine does, but more slowly. It is used in the color industry and organic laboratory, and is the source from which its compounds are prepared.

Hydrogen Bromide, HBr, may be formed by the direct union of hydrogen and bromine, equal volumes of bromine vapor and hydrogen uniting to form hydrogen bromide without change of volume. If we attempt to prepare hydrogen bromide in a manner similar to that used in the preparation of hydrogen chloride, — by the action of strong sulphuric acid on a bromide, — bromine and sulphur dioxide, as well as hydrogen bromide, are

evolved. This shows that hydrogen bromide is less stable than hydrogen chloride, and acts as a reducing agent on sulphuric acid. The reactions which occur are represented in these equations:
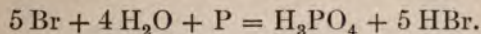
$$NaBr + H_2SO_4 = NaHSO_4 + HBr;$$
$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$
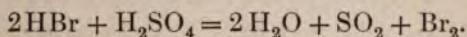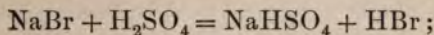
Pure hydrogen bromide in solution can, however, be prepared by the action of the bromides of phosphorus on water. In practice, the phosphorus bromides are not actually prepared, but bromine is added slowly to a mixture of red phosphorus and water:

$$5Br + 4H_2O + P = H_3PO_4 + 5HBr.$$

Other ways of preparing the solution of hydrogen bromide are by leading hydrogen sulphide into bromine covered by water:

$$Br_2 + H_2S = 2HBr + S;$$
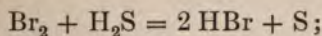
or by the action of sulphur dioxide on bromine water:

$$Br_2 + 2H_2O + SO_2 = 2HBr + H_2SO_4.$$
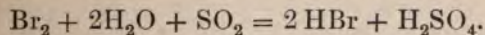
This reaction is reversed in the presence of strong sulphuric acid, as is shown above (*cf.* p. 69).

Hydrogen bromide is a colorless, fuming gas which resembles hydrogen chloride in all respects. It is 2.71 times as heavy as air, and one liter of it weighs 3.50 grams. On analysis, its composition is found to be, hydrogen, 1.25 per cent, and bromine, 98.75 per cent. From these facts its formula HBr is derived. Its solution in water is called **hydrobromic acid**, and, when boiled, behaves like hydrochloric acid. The bromides

of the metals, like the chlorides, are mostly soluble, but silver bromide, like silver chloride, is insoluble, and is therefore precipitated when silver nitrate is added to a solution of a bromide.   Potassium bromide is used in medicine, and silver bromide is the chief sensitive compound on the photographic dry plates.   Bromine forms no compounds with oxygen; but two unstable oxyacids, hypobromous acid, $HBrO$, and bromic acid, $HBrO_3$, corresponding to two of the oxychlorine acids, are known, and form hypobromites and bromates which resemble the hypochlorites and chlorates.

Bromine is readily recognized by its color and odor, and is detected in its compounds by the reactions used in its preparation.   Even small quantities may be detected by the fact that when an aqueous solution containing bromine is shaken with a little chloroform or ether, these liquids, which are nearly insoluble in water, remove the bromine from the water, forming yellow solutions.

IODINE

Formerly, a considerable part of the world's supply of soda (sodium carbonate), used for soap and glass making, was obtained from seaweed.   By burning the dried seaweed, the sodium salts which they contained were mostly converted into carbonate.   This was separated from the insoluble matters by washing the ashes with water, and recovered by evaporation.   In the mother liquor of this industry, Courtois, a manufacturer of saltpeter, discovered in 1812 that there were substances which, on treatment with chlorine or with maganese dioxide and sulphuric acid, yielded a kind of

matter previously unknown and which proved on further examination to be an elementary substance. It was called **iodine** from the Greek word describing the violet color of its vapor. Iodine compounds are widely distributed, accompanying those of chlorine and bromine in very small quantities. Only minute amounts are contained in sea water, but they are absorbed and stored up by seaweed, especially by the deep-growing varieties; they are present in most salt deposits and in few minerals; in crude Chile saltpeter; in some land plants, and in many sea animals, as in oysters and sponges. Ever since its discovery in the ashes of seaweed, iodine has been obtained from this source in the same way that bromine is obtained from the mother liquor of salt works, *i.e.*, by the action of manganese dioxide and sulphuric acid, or of chlorine.

As in the ordinary process of burning seaweed some of the iodine was lost by volatilization, the dried weed is now carbonized in retorts. Gases and tar come off, and the iodides are dissolved from the residue. In a still more recent process, the iodine compounds are dissolved out of the weed without previous charring. In this way less iodine is lost, and the seaweed is worked up into algin, which is a sort of gelatine.

The chief source of iodine at present, however, is crude Chile saltpeter, in which it occurs chiefly as iodate of sodium. The mother liquor left from the purification of the saltpeter by crystallization is treated with acid sulphite of sodium, which sets the iodine free.

The crude iodine contains bromine and chlorine, from which it is freed by mixing it with potassium iodide and heating. The chlorine and bromine react with

the potassium iodide to form the chloride and bromide, while the iodine of the salt is liberated, and all of the iodine sublimes, condensing from the state of vapor in crystalline form.

Properties. — Iodine is a solid resembling graphite in color and luster. It is nearly five times as heavy as water, volatilizes slowly at room temperature, melts at about the same temperature as sulphur, and boils at 183°–184°. The violet color of the vapor is due to admixture with air; when pure, the color is a deep blue. Iodine vapor is one of the heaviest known, being 8.7 times as heavy as air. Its density below 700° corresponds to a molecule consisting of two atoms, I_2. At higher temperatures the density becomes less, and at 1700° indicates a monatomic molecule.

Iodine dissolves very slightly in water, coloring it brown. The oxidizing power of the solution is much less than that of chlorine or bromine water. It is more readily soluble in alcohol (tincture of iodine), and dissolves freely in chloroform, ether, and a number of other liquids; and these may be used to remove it from its solution in water by shaking the two together. It is also very soluble in an aqueous solution of potassium iodide, and this solution is used in medicine. Its chemical properties are in general like those of chlorine and bromine, but its compounds with hydrogen and with the metals are less stable than those of bromine. It does not combine readily with hydrogen, but unites vigorously with phosphorus, even when solid; and with finely divided zinc or iron, in contact with water, it forms iodides. Its most characteristic reaction is that of producing a fine blue color with starch paste.

This serves to identify iodine, and is also a test for starch.

Hydrogen iodide, HI, is oxidized by sulphuric acid so easily that it cannot be prepared by the reaction of this acid on iodides, for the hydrogen iodide is almost completely oxidized to iodine with the formation of sulphur dioxide. Its solution is usually prepared by reactions similar to those employed for making hydrogen bromide.

Hydrogen iodide closely resembles hydrogen chloride and hydrogen bromide, but is much less stable. It is easily decomposed by heat into hydrogen and iodine and cannot be formed by the direct union of these elements. Its aqueous solution is called **hydriodic acid**, and yields, on distillation, an acid of constant composition which boils at 127°. When the solution is exposed to the air, it becomes brown from the oxidation of hydrogen iodide and liberation of iodine. On account of the instability of hydrogen iodide, its solution acts as a reducing agent, and is often used in this way. The iodides are analogous to the chlorides and bromides. Insoluble silver iodide is precipitated when a solution of silver nitrate is added to their solutions. Most of the iodides are decomposed by heat, and are slowly oxidized in solution when exposed to the air.

Hypoiodous acid, HIO, and **Iodic acid**, HIO_3, and their salts are similar to the corresponding compounds of chlorine and bromine. **Periodic acid** has the formula H_5IO_6 or $(HO)_5IO$, in which iodine is heptavalent. Salts of this acid and of other acids derived from it by subtracting the elements of water are known. Iodine forms but one stable oxide, I_2O_5, the **anhydride** of iodic acid.

The oxygen compounds of iodine are much more stable than those of chlorine and bromine, and potassium iodate may be made by the action of iodine on the chlorate:

$$2 \, KClO_3 + I_2 = 2 \, KIO_3 + Cl_2.$$
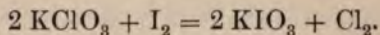
Iodine in solution in alcohol (tincture of iodine), or in a solution of potassium iodide, in which it is very soluble, is employed in medicine as a counter-irritant, and for other purposes. Silver iodide, like the silver chloride and bromide, is sensitive to light and is used in photography.

FLUORINE

When the minerals fluorspar or cryolite are heated with concentrated sulphuric acid, a gas is given off which, like hydrogen chloride, fumes in the air, and has a sharp acid smell; but which also, unlike any other known gas, attacks glass and porcelain readily at ordinary temperatures. The preparation of this gas should be conducted in lead or platinum vessels. The gas dissolves freely in water, forming a strongly acid solution which can be preserved in bottles of wax. In 1810 this acid was shown to be analogous to hydrochloric acid, forming salts which are like the chlorides. On this account, the gas was considered to be a compound of hydrogen and some element of the general character of chlorine. All attempts to isolate this element proved unsuccessful until the latter part of the century, but it was named fluorine from the fluorspar from which its compounds were obtained, and its atomic *weight* was determined by finding its equivalence to the

SO_4 group in the reaction by which it was made,[1] and assuming, by analogy with chlorine, that it was a monovalent element. The reaction for the preparation of the acid gas is represented thus:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$
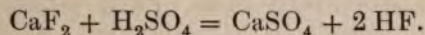
In 1886, Moisson succeeded in solving the difficult problem of obtaining free fluorine by the electrolysis of perfectly anhydrous liquid hydrogen fluoride.

Properties. — Fluorine is a greenish yellow gas, lighter in color than chlorine, with an odor fainter than that of chlorine and resembling that of bleaching powder. It is the most active elementary substance known; it unites explosively with hydrogen even in the dark, and decomposes water vigorously with the formation of hydrofluoric acid and ozone. It unites with most metals, forming fluorides, and even carbon in the form of lampblack burns in it. Oxygen, chlorine, and nitrogen do not combine with it. It displaces chlorine from solid chlorides, and also displaces bromine and iodine from their salts, and at the same time unites with them.

Hydrogen Fluoride, HF, can be obtained as an anhydrous liquid by taking great precautions to exclude every trace of moisture during its preparation. It boils at $19.4°$. It is a very dangerous and poisonous liquid, and even when diluted with water, it turns the flesh white and produces wounds which heal very slowly. Both the gas and its solution etch glass and are commonly used for this purpose. The glass is first prepared by covering it with a film of paraffine. The design is drawn with a sharp point which lays bare the glass in

[1] "Quantitative Experiments," page 87.

the lines where it is to be etched. The glass is then exposed face down over the lead vessel in which the gas is generated ; or a solution of the acid is brushed over the lines. The gas etches with a ground glass effect, while the solution leaves smooth depressions which are not readily seen unless filled with pigment, as in chemical thermometer scales, etc. The etching is due to the fact that hydrofluoric acid acts on the silicon, which is one of the constituents of glass, with the formation of a gaseous fluoride of silicon. Other silicon compounds are also decomposed by hydrofluoric acid, and it is used on this account in the analysis of silicate minerals which are not attacked by other acids.

The vapor density of hydrogen fluoride up to $30°$ corresponds to the formula H_2F_2. Above $30°$ the density diminishes, and above $88°$ indicates that the molecules are HF. The action of hydrofluoric acid on such metals as zinc and magnesium is less vigorous than that of hydrochloric acid ; and it forms many acid salts, such as KHF_2. These facts are what we might expect from its double formula.

The fluoride of silver, unlike the other silver halides, is soluble in water ; and most of the fluorides are soluble, except those of calcium, strontium, and barium.

Detection of Fluorine. — The presence of fluorine in its compounds is detected by etching glass with the hydrogen fluoride which is given off when they are heated with concentrated sulphuric acid ; or by the fact that silicon fluoride, which is formed when a fluorine compound and sand are heated with sulphuric acid, is a gas which gives a white precipitate with a drop of water (p. 203).

Quantitative Experiments with the Halogens. — The following experiments may be made for finding the equivalents of the halogens, or for determining the formulas of their compounds: Synthesis of the chloride, bromide, or iodide of silver; synthesis of calcium fluoride; conversion of calcium fluoride into sulphate (see *Quantitative Experiments*).

If the members of this group are arranged in order according to any one property, it will be seen that the variations of their other properties follow the same order. Thus, the color deepens as we go from fluorine through chlorine and bromine to iodine; the physical state changes from gas through liquid to solid, and the specific gravity increases in the same order; the chemical affinity for hydrogen and the metals decreases, while that for oxygen increases. It is to be noticed, further, that the order in which they are arranged by their properties is also the order of their atomic weights. Other groups of elements showing similar gradations of properties in the order of their atomic weights are known, a fact which much simplifies the study of chemistry. And not only is this the case, but it has been found that if all of the elements are arranged in the order of their atomic weights, a more or less satisfactory coördination of properties and atomic weights may be shown (see Chapter XXXIV).

K

CHAPTER XIII

NITRIC ACID AND OXIDES OF NITROGEN

COMPOSITION OF SALTPETER AND NITRIC ACID

SALTPETER is a well-known substance which is an ingredient of black gunpowder, and is used in making fireworks, for preserving meat, and other purposes. It is found as an efflorescence on the soil in hot, dry countries, where it has been formed by the decomposition of animal matter in the presence of potash, and has been obtained from this source, and made artificially in enormous amounts, to supply the demand for gunpowder. A closely related substance, known as Chile saltpeter, is found in great deposits in Chile and Peru, and is used as a fertilizer and for making the other saltpeter and nitric acid. When examined by the flame coloration and the spectroscope, Chile saltpeter is found to contain sodium, and the other, potassium. Except for this difference, their composition is the same, as is shown by the following experiments, which may be made with either of them.

When saltpeter is heated in a test tube it melts, and at a higher temperature decomposes with the evolution of oxygen, which is detected by the rekindling of a spark. If a piece of charcoal is dropped into the melted saltpeter, it burns brightly; and after the reaction, carbon dioxide is present in the test tube, as is

shown by means of a drop of limewater on a glass rod. If sulphur is used instead of charcoal, the residue, after cooling and dissolving in water, responds to the test for a sulphate.   These experiments prove that saltpeter contains oxygen and is an oxidizing agent when heated. If saltpeter is heated with finely divided iron, a gas is given off which is identified as nitrogen by the fact that it extinguishes flame and does not render limewater milky.   Saltpeter contains, therefore, nitrogen, oxygen, and potassium (or sodium).   No water appears in the experiments we have made, if the materials are first well dried, and we may therefore conclude that hydrogen is not one of the constituents.   A synthesis of saltpeter can be made by passing electric sparks through air, over potassium hydroxide.   The volume of confined air slowly diminishes from the production of oxides of nitrogen which are absorbed in the solution, and by addition of oxygen may be made wholly to disappear, with the exception of a small bubble of argon gases.   (This is a method for obtaining argon from air, and Cavendish, who first carried it out, noted the residual bubble, though the recognition of it as a new elementary gas was not made till more than a hundred years later.) From the solution a small amount of saltpeter crystals can be obtained.   This experiment, together with the analytical experiments, shows that nitrogen, oxygen, and potassium are the only constituents of saltpeter.

When saltpeter is gently heated with concentrated sulphuric acid, fuming, acid vapors are given off, which condense at room temperature to an acid, corrosive liquid.   This acid liquid is called nitric acid from "niter," an old and still-used name for saltpeter.

If we now represent the results of our experiments by a tentative equation, letting x stand for the group of nitrogen and oxygen atoms which are present in saltpeter and probably in nitric acid, we have :

$$Kx + H_2SO_4 = KHSO_4 + Hx.$$
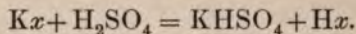
Nitric acid mixes with water in every proportion, and it and its solutions act vigorously on most metals. The reaction with metals produces, however, no hydrogen gas as in the case of sulphuric and hydrochloric acids. Brown gases usually appear, though the dilute acid with zinc or magnesium may give no gas at all. We have, therefore, no direct proof that hydrogen is a constituent of the acid. But nitric acid, like the saltpeter from which it is made, is a strong oxidizing agent. This is shown by the charring of sugar or sawdust when warmed with the concentrated acid, and by its conversion of sulphur into sulphuric acid. It is fair to infer that in the action of nitric acid on metals, the hydrogen reduces the acid, as sulphuric acid is reduced under certain conditions (p. 90). We shall have, later, indirect evidence that the acid does contain hydrogen (p. 150). The composition of the group "x" in our formula will appear in the following discussion.

Formulas of Nitric Acid and Saltpeter. — We may find formulas for these compounds by a method like that employed with sulphuric acid and the sulphates. If a known weight of silver is dissolved in nitric acid and the solution evaporated to dryness, and heated until all acid odor has disappeared, it will be found that the weight of the silver nitrate is 1.575 times as much as

that of the silver it contains [1].   Since the atomic weight
of silver is 107.88, the sum of the atomic weights of the
nitrogen and oxygen in silver nitrate is found by the
proportion :

$$1 : 0.575 : : 107.88 : x$$

from which $x = 62$ (very nearly).   Now the only com-
bination of the atomic weights of nitrogen and oxygen,
which will add up 62, is NO_3 ($N = 14$, and $O_3 = 48$).
We therefore infer that the acid group of nitric acid is
NO_3 and that the formula of silver nitrate is $AgNO_3$.
Therefore, since silver is a monad element, the formula
of nitric acid is HNO_3.   The formulas of the saltpeters
are, then, KNO_3 and $NaNO_3$.

Another experiment which enables us to verify these
conclusions may be made by heating a known weight
of saltpeter with iron, and determining the amount of
nitrogen which is evolved.[2]   The result will give about
13.86 per cent of nitrogen, which agrees with the per cent
reckoned from the formula KNO_3.

Nitric Acid. — In the preparation of nitric acid on a
large scale, Chile saltpeter, $NaNO_3$, is used because it is
the cheapest nitrate.   The reaction is :

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$
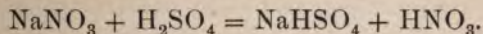
The acid sulphate $NaHSO_4$ can react with more salt-
peter, giving more nitric acid :

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$
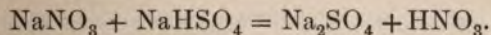
This second reaction is usually not carried out, as it
requires a higher temperature, and is attended with some
decomposition of the acid.

[1] " Quantitative Experiments," page 78.
[2] *Ibid.*, page 81 ; *cf.* also page 82.

Properties. — Pure nitric acid is a colorless liquid which fumes in the air, and boils at 78.2° with partial decomposition, oxides of nitrogen being formed which dissolve in the acid and color it yellow, while water, produced at the same time, dilutes the acid. A similar decomposition takes place when the pure acid or a strong solution is exposed to sunlight. The acid mixes in every proportion with water, and the solutions when heated behave like those of hydrochloric acid, — both strong and weak solutions finally giving an acid of constant boiling point and constant composition, which, however, varies with changes of pressure and is not a chemical compound.

Chemically, nitric acid is a strong acid and also a powerful oxidizing agent. When it acts on metals, nitrates are produced, and simultaneously part of the acid is reduced to oxides of nitrogen, nitrogen, or even to ammonia.

Phosphorus, sulphur, carbon, and many organic substances are oxidized by the concentrated acid. With many hydrocarbons the acid brings about a replacement of the NO_2 group for hydrogen, with the formation of so-called **nitro-compounds**. Many of the nitro compounds are colored yellow, and the production of a yellow color in wool and other animal substances is characteristic of this acid. With other organic substances which contain hydroxyl groups, and belong to the class of alcohols, nitric acid forms compounds which are analogous to salts, the place of the metal being taken by a group of carbon and hydrogen atoms. Among these organic nitrates or " ethereal salts " are glycerine nitrate, commonly known as nitroglycerine, and nitrates of cellulose, which form collodion, gun-cotton, and smokeless powder. A mixture

of nitric and hydrochloric acids is called **aqua regia**, because of its power of dissolving the " noble " metals, such as platinum and gold, which are not attacked by either acid alone. When heated, aqua regia evolves chlorine from oxidation of the hydrochloric acid, and its solvent power lies in this fact, the nascent chlorine uniting with the metals to form chlorides.

The nitrates of all the metals, except those of the alkalies, break up when heated, giving oxides of nitrogen and oxides of the metals, or in a few instances, the metal itself. All normal nitrates are soluble, and consequently no test for the nitric acid group NO_3 by precipitation can be made, as in the case of sulphuric and hydrochloric acids. But the presence of this group is easily detected by the brown vapors which appear when the acid, or a mixture of a nitrate and sulphuric acid, is heated with copper. Minute amounts are detected by the fact that the acid is reduced by ferrous sulphate, and the nitric oxide, which is the reduction product, unites with the sulphate to form a dark-colored compound.

Nitrous Acid and Nitrites. — We have seen that when saltpeter is heated it loses oxygen. If the proportion of this oxygen is determined, it is found to be about one third of the oxygen in saltpeter. This corresponds to the loss of one atom of oxygen from the salt, and the substance which remains is **potassium nitrite**, KNO_2, a salt of **nitrous acid**, HNO_2. Nitrous acid, like sulphurous acid, exists only in solution. The nitrites, however, like the sulphites, are stable salts. Nitrites are formed by reduction of nitrates, as when potassium nitrate is heated alone or with lead or copper :

$$KNO_3 + Pb = KNO_2 + PbO.$$
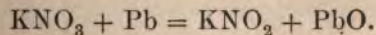
Nitrous acid is easily oxidized to nitric acid and is also readily reduced. Nitrites give brown fumes at once with dilute acids, and are thus distinguished from the nitrates. An unstable hyponitrous acid, $H_2N_2O_2$, and its salts are also known.

OXIDES OF NITROGEN

The oxides of nitrogen and their relations to the acids are shown in the following table:

Nitrous oxide,	N_2O	Hyponitrous acid,	$H_2N_2O_2$
Nitrous anhydride,	N_2O_3	Nitrous acid,	HNO_2
Nitric oxide,	NO	. . . .	
Nitrogen tetroxide,	N_2O_4	. . . .	
and	NO_2		
Nitric anhydride,	N_2O_5	Nitric acid,	HNO_3

Two of the five oxides of nitrogen are anhydrides of nitric and nitrous acids, and all, except the nitric anhydride, may be formed by the reduction of nitric acid.

Nitrogen Pentoxide or Nitric Anhydride, N_2O_5, is made by distilling a mixture of anhydrous nitric acid and phosphorus pentoxide. The elements of water are withdrawn from the nitric acid and unite with the phosphorus pentoxide to form the non-volatile phosphoric acid. Nitric anhydride crystallizes out from the distillate when this is cooled. It is a colorless solid which unites immediately with water to form nitric acid, and is a powerful oxidizing agent, decomposing readily into lower oxides of nitrogen and oxygen.

**Nitrogen Tetroxide,** N_2O_4 and NO_2, is the chief constituent of the reddish brown fumes produced by the

decomposition of nitric acid or nitrates.   It may be formed by the direct union of two volumes of nitric oxide and one of oxygen:

$$2\,NO + O_2 = N_2O_4;$$
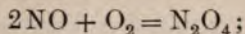
or prepared by heating copper or lead nitrate:

$$2\,Pb(NO_3)_2 = 2\,PbO + 4\,NO_2' + O_2.$$
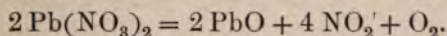
Nitrogen tetroxide is a liquid boiling at 22°.   The vapor becomes darker as the temperature is higher, and density determinations show that the molecular weight at the lower temperatures is represented by N_2O_4, but that it gradually dissociates, as the temperature rises, into molecules whose formula is NO_2.   It dissolves and decomposes in water.   In a small amount of cold water it gives nitrous and nitric acids:

$$N_2O_4 + H_2O = HNO_3 + HNO_2;$$
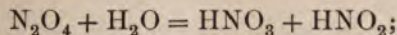
while in warmer water or with an excess of water it forms nitric acid and nitric oxide:

$$3\,N_2O_4 + 2\,H_2O = 4\,HNO_3 + 2\,NO.$$
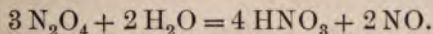
It is a strong oxidizing agent, being readily reduced to nitric oxide, NO.   Nitrogen tetroxide is also called nitrogen peroxide and nitrogen dioxide.

Nitrous Anhydride, N_2O_3, is the next reduction product of nitric acid.   It is difficult to obtain it unmixed with other oxides.

Nitric Oxide, NO. — When diluted nitric acid is added to copper in a flask provided with a delivery tube, the brown vapors which at first appear are gradually driven out, and a colorless gas is evolved, which can be col-

lected over water. A purer gas may be obtained by absorbing the gas in ferrous sulphate solution and then driving it off by heating. Nitric oxide forms an unstable dark-colored compound with the ferrous sulphate. Its most striking property is that of immediately giving reddish brown fumes of the tetroxide when mixed with air or oxygen. Its density is 1.038 (air = 1), which indicates a molecular weight of about 28, corresponding to the formula NO. A burning candle and burning sulphur are extinguished in nitric oxide; but phosphorus, if already burning brightly, continues to burn with great brilliancy. From these facts it may be inferred that combustions in nitric oxide are really combustions in oxygen diluted with an equal volume of nitrogen, the high temperature necessary to start the combustion effecting the decomposition of the gas into its constituents.

Nitric oxide acts in the lead chamber process of making sulphuric acid as a carrier of oxygen from the air admitted to the chambers to the sulphurous acid, being oxidized by the air, and reduced by the sulphurous acid as this is oxidized to sulphuric acid.

Nitrous Oxide. — The lowest oxide of nitrogen produced by the reduction of nitric acid is nitrogen monoxide, or nitrous oxide, which is shown by its density, 1.53 (air = 1) to have the formula N_2O. It is almost always prepared by heating ammonium nitrate, which splits into water and nitrous oxide:

$$NH_4NO_3 = 2 H_2O + N_2O.$$
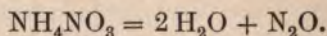
Nitrous oxide is a colorless gas of slight, but agreeable, taste and odor. It is rather soluble in water. It is

quite easily liquefied, and is supplied commercially in the liquid state in cylinders.   It supports combustion with about the same vigor as oxygen, and, like oxygen, rekindles a spark.   Sulphur which has just been kindled is, however, extinguished.   Nitrous oxide may be distinguished from oxygen by the fact that, when mixed with nitric oxide, no brown fumes are produced, while they appear at once when oxygen and nitric oxide come together.

The gas is used as an anæsthetic in dentistry and minor surgical operations.   It is commonly called "laughing gas" because it produces a transient nervous excitement when inhaled.
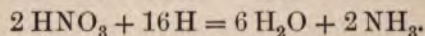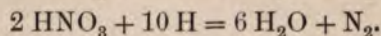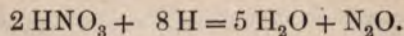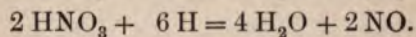
Reductions of Nitric Acid. — When nitric acid acts on metals, the nascent hydrogen which is produced by the immediate reaction interacts with the excess of acid, reducing it to an extent which depends on the concentration of the acid, the temperature, and the character of the metal employed.   Metals which, like copper, do not evolve hydrogen from dilute sulphuric and hydrochloric acids, may, nevertheless, be supposed to enter into a strongly reversible reaction with nitric acid:

$$Cu + 2\,HNO_3 \rightleftarrows Cu\,(NO_3)_2 + 2\,H.$$
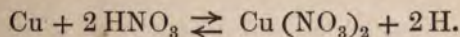
The nascent hydrogen, in the presence of the readily oxidizable nitric acid, combines with its oxygen to form water, and, consequently, the reaction goes on to completion in the direction from left to right in the above equation.   With more active metals, such as zinc or magnesium, the reducing action is greater than with copper, and some hydrogen may be evolved.   The metal

may be considered to act as a contact agent and thus influence the extent of the reduction.

The possible reductions of nitric acid by nascent hydrogen may be indicated by the following equations:

$$2\,HNO_3 +\ \ 2\,H = 2\,H_2O + N_2O_4 \text{ or } 2\,NO_2.$$
$$2\,HNO_3 +\ \ 4\,H = 3\,H_2O + N_2O_3.$$
$$2\,HNO_3 +\ \ 6\,H = 4\,H_2O + 2\,NO.$$
$$2\,HNO_3 +\ \ 8\,H = 5\,H_2O + N_2O.$$
$$2\,HNO_3 + 10\,H = 6\,H_2O + N_2.$$
$$2\,HNO_3 + 16\,H = 6\,H_2O + 2\,NH_3.$$
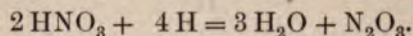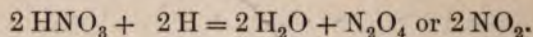
The chief product which is observed with copper and other inactive metals is nitric oxide, which at once gives brown vapors of the tetroxide as it comes into the air.   When ammonia is formed, it immediately unites with the excess of acid to make ammonium nitrate, which remains in solution.

Valence of Nitrogen in its Oxides. — Application of the rule for finding valences (p. 102) would give us valences for nitrogen in its five oxides which range from one to five.   It is, however, usually assumed that in nitrous oxide two trivalent nitrogen atoms are in partial combination with each other, as shown in the graphic

formula, $\begin{matrix} N\diagdown \\ \parallel \ \ \diagup O. \\ N\diagup \end{matrix}$ In nitric oxide, nitrogen must be diva-

lent; in nitrous anhydride, it is trivalent; in the tetroxide, tetravalent; and in nitric anhydride, pentavalent.   Nitric acid and nitrous acid are both hydroxyl compounds, like all other oxyacids, and their graphic

formulas are $H-O-N\diagup_{O}^{O}$ and $H-O-N=O$, in which the nitrogen is pentavalent and trivalent, respectively.

COMPOUNDS OF NITROGEN WITH THE HALOGENS

Nitrogen Halides. — When chlorine is led into a warm solution of ammonium chloride, drops of a yellowish oil separate out, which is exceedingly explosive. This substance is decomposed quietly by a solution of ammonia with the formation of ammonium chloride and nitrogen, and has in this way been successfully analyzed. Its composition is found to be represented by the formula NCl_3, **nitrogen chloride.** It explodes in sunlight, and when brought in contact with phosphorus, iodine, turpentine, and some other substances.

Similar explosive compounds of nitrogen with bromine and with iodine can be made. The iodine compound is a black solid, and may be made for experiment by pouring a concentrated ammonia solution on powdered iodine on a filter. When dry, it explodes by the touch of a feather. These compounds all decompose gradually in cold water.

CHAPTER XIV

AMMONIA; NITROGEN

AMMONIA

Ammonia water or aqua ammonia, which is used in the household as a cleansing agent, has a strong alkaline reaction. It has a well-known pungent odor, and on heating gives off ammonia gas which turns moistened litmus paper blue, and gives a white cloud when a rod wet with strong hydrochloric acid is brought into it. The gas is extremely soluble in water, so that it must be collected for experiment over mercury, or, as it is much lighter than air, by upward displacement of air. The gas was first isolated by Priestley in 1774 by collection over mercury, and called by him "alkaline air." It is the only alkaline gas we find in inorganic chemistry.

Composition of Ammonia. — When ammonia is tested with a lighted candle, there is a momentary flare of yellow flame and the candle goes out without kindling the gas. Although incombustible under ordinary conditions, ammonia will burn when mixed with oxygen. If ammonia and oxygen are fed to the mixing jet of a blast lamp, the gases can be ignited and will burn with a yellow flame. On holding a bell jar over the flame, moisture is deposited on the glass. This shows that hydrogen must be one of the constituents of ammonia. If, acting on this knowledge, we lead ammonia through a tube containing heated copper oxide, we find that the

copper oxide is reduced, water is formed, and a gas
issues from the delivery tube which is insoluble in
water.   On collecting the gas, it is found to be nitrogen.
The presence of hydrogen as a constituent of ammonia
can be directly confirmed by leading the gas through a
tube containing heated magnesium, when a gas is set
free which is readily identified as hydrogen.   Inciden-
tally, we find that, if the magnesium-nitrogen compound
formed in the tube is put into water, ammonia is repro-
duced. Ammonia, then, contains hydrogen and nitrogen.
That these are its only constituents appears from the
results of the analysis by copper oxide, and may be di-
rectly proved by passing electric sparks through a mix-
ture of nitrogen and hydrogen standing over water.
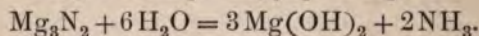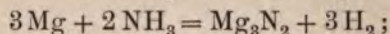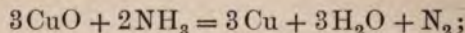The gases gradually disappear and the water contains
ammonia.

Formula of Ammonia. — By carrying out the experi-
ment with copper oxide described above, in a quanti-
tative way, we may determine the proportions of the
constituents of ammonia.[1]   The weight of the nitrogen
which is collected is found, and the weight of the hydro-
gen is calculated from the loss of weight of the copper
oxide, — that is, from the oxygen with which it has
combined to form water.   The results show that the
composition of ammonia is: hydrogen 17.75 per cent,
and nitrogen 82.25 per cent.   Dividing these figures by
the respective atomic weights, we obtain an atomic ratio
of three to one, and arrive at the empirical formula, NH_3.
On determining the weight of ammonia, we find that
one liter weighs about 0.77 gram, or that it is about
0.6 times as heavy as air.[2]   From these figures we find

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[1] " Quantitative Experiments," page 49.   [2] *Ibid.*, page 36.

that the molecular weight must be about 17, which shows that NH_3 is also the molecular formula. Using this formula, we may write equations for the reactions that have been made:

$$3\,CuO + 2\,NH_3 = 3\,Cu + 3\,H_2O + N_2;$$
$$3\,Mg + 2\,NH_3 = Mg_3N_2 + 3\,H_2;$$
$$Mg_3N_2 + 6\,H_2O = 3\,Mg(OH)_2 + 2\,NH_3.$$

Volumetric Composition. — The relation of the volume of ammonia to the volumes of the hydrogen and nitrogen which compose it may be found as follows: If sparks from an induction coil are passed through a measured volume of ammonia confined by mercury, the volume is nearly doubled. On introducing a little water or acid, very little change in volume occurs, showing that the ammonia was nearly all decomposed into hydrogen and nitrogen. Therefore the sum of the volumes of these gases is twice that of the volume of ammonia formed by their combination. Further, if mixtures of hydrogen and nitrogen in different proportions are made and confined over sulphuric acid, and induction sparks are passed through them, it is found that the volume diminishes and that the gases disappear completely when the volume of hydrogen is three times that of the nitrogen. In this case, ammonia is formed and absorbed by the acid. The conclusion we draw from these experiments is that three volumes of hydrogen and one volume of nitrogen — four volumes — unite to form two volumes of ammonia. If we represent these facts as we did those in regard to the volumetric composition of steam and of hydrogen chloride, we have:

1000	1000	1000	+	1000	=	1000	1000

Hydrogen   Nitrogen   Ammonia
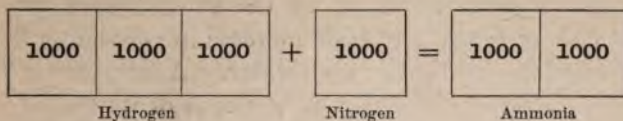
or in a molecular equation: $3\,H_2 + N \rightleftarrows 2\,NH_3$.

This reaction is a reversible one. With ammonia or with a mixture of hydrogen and nitrogen over mercury, equilibrium is reached when there is 2 per cent of ammonia. Hence the decomposition of ammonia by the induction spark is nearly complete. But when we start with the mixture of hydrogen and nitrogen over acid, the ammonia is removed as fast as it is formed by absorption in the acid, and so the reaction goes to completion in this direction.

These volumetric relations may be found in another way, which is easily carried out. When a known volume of chlorine is brought in contact with a strong solution of ammonia, the chlorine unites with the hydrogen, setting free a volume of nitrogen equal to one third of its own volume.[1] Since we know that hydrogen and chlorine combine in equal volumes (p. 107), we may infer that the composition of ammonia by volume is three volumes of hydrogen to one volume of nitrogen :

$$2\,NH_3 + 3\,Cl_2 = N_2 + 6\,HCl.$$
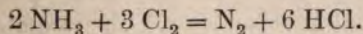
Properties of Ammonia. — The solubility of ammonia in water is very great. At 0° water absorbs nearly 1300 times its own volume of ammonia, and at ordinary temperature (20°) about 700 times its volume. The

[1] " Quantitative Experiments," page 51 ; see also page 52.

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absorption is accompanied by the evolution of much
heat; there is also a notable increase in volume, so that
the solutions are lighter than water.   A saturated solu-
tion at 20° contains about 35 per cent of its weight of
ammonia and has a specific gravity of 0.882.   The gas
is completely driven off from its solution when this is
boiled.   Ammonia can be rather easily liquefied by
cold ($-40°$) or pressure, and liquid ammonia is sold
in cylinders.   Liquid ammonia boils at $-38.5°$, and in
changing to the state of gas absorbs more heat than
any other easily liquefied gas.   These facts, together
with the great solubility of ammonia in water, have
led to its extensive employment as a means of produc-
ing artificial cold.   For this purpose ammonia is driven
off from a concentrated solution by heat and liquefied
under its own pressure; then it is allowed to evaporate
and is absorbed in cold water.   The heat necessary for
its evaporation is taken from the substances in contact
with the vessel which contains it, and in this way water
may be frozen, or brine which is circulating in pipes
through a cold storage room may be chilled and cool
the air of the room.

We have noticed the alkaline reaction of ammonia
and the fact that it combines directly with hydrogen
chloride.   These two gases unite in equal volumes to
form a crystalline powder which resembles common
salt.   Since we know the formulas of both of the gases,
the following equation will represent the reaction:

$$NH_3 + HCl = NH_3HCl \text{ or } NH_4Cl.$$
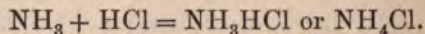
The solution of ammonia is also alkaline, and neu-
tralizes acids.   On evaporation of the neutralized solu-

tions, solid salts are obtained. In these the group NH_4 plays the same part that sodium and other metals do in their salts; and consequently, the group is named, in analogy with the metals, **ammonium**. Further, on account of its alkaline reaction and its power of reacting with acids to form salts, the solution of ammonia is supposed to contain **ammonium hydroxide**, a base and a hydroxyl compound of ammonium, which is given the formula NH_4OH, in analogy with sodium hydroxide, etc. Ammonium hydroxide is too unstable to be obtained by itself, breaking up, when its solution is evaporated, into water and ammonia. Nor is the group NH_4 capable of independent existence, though an amalgam of it with mercury may be formed, which quickly decomposes into mercury, ammonia, and hydrogen (p. 274). Ammonium is readily displaced from its salts by other bases, giving ammonium hydroxide which, on heating, gives ammonia and water.

$$NH_4Cl + NaOH = NaCl + NH_4OH;$$
$$NH_4OH = NH_3 + H_2O.$$
$$2\,NH_4Cl + Ca\,(OH)_2 = CaCl_2 + 2\,NH_3 + 2\,H_2O.$$
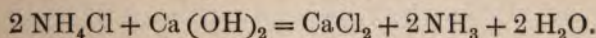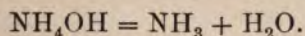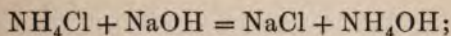
The second reaction, with slaked lime, is commonly employed for the preparation of ammonia from the ammonium salts. The ammonium salts all volatilize when heated, separating into ammonia and the acid, or undergoing further decomposition. The nitrate and the nitrite of ammonium decompose when heated as follows:

$$NH_4NO_3 = 2\,H_2O + N_2O;$$
$$NH_4NO_2 = 2\,H_2O + N_2.$$
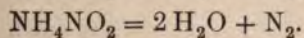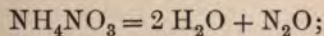
These reactions are employed for the preparation of nitrous oxide and of nitrogen. It will be found usually in the decomposition by heat of compounds containing hydrogen and oxygen, that these elements unite to form as much water as possible. This tendency to form water may be regarded as determining the character of the reactions.

Dissociation of Ammonium Chloride. — Ammonium chloride sublimes without apparent change. But it can be shown that while in the state of vapor it is more or less separated or dissociated into ammonia and hydrogen chloride. If a strip of moistened blue litmus paper is placed across the mouth of a test tube containing a little ammonium chloride, the litmus paper turns red when the salt is heated. If the tube is now withdrawn from the flame, the paper presently becomes blue again. During the heating the lighter ammonia escapes more rapidly than the hydrogen chloride, leaving the current of vapor acid; then, when no more vapor is supplied by heating, the more rapid diffusion of the ammonia brings an excess of this gas to the mouth of the tube. Ammonium chloride vapor, being a mixture with the two gases which unite to form the salt, has a vapor density less than that which the undissociated salt vapor would have. If the dissociation were complete, the volume would be double that of undissociated vapor, and the density half that of ammonium chloride. The molecular equation shows the doubling of the volume:

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$
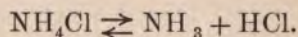
The molecular weight of ammonium chloride derived from its vapor density is, therefore, much less than the

value, 53.50, which must be assigned to it on other grounds.   At a high enough temperature to produce complete dissociation it would evidently be half as large, or the average of the molecular weights of ammonia and hydrogen chloride.

The vapor density method of finding molecular weights fails, therefore, in cases where dissociation occurs.

Reactions of Ammonia with Metals. — We have seen that ammonia is decomposed by heated magnesium with the production of a nitride of magnesium and hydrogen.   It acts on some other metals in a similar way, but not always with the liberation of all of its hydrogen.   On heated sodium or potassium, for instance, the reaction gives a compound in which the metal replaces only one atomic weight of hydrogen:

$$2\,Na + 2\,NH_3 = 2\,NaNH_2 + H_2.$$
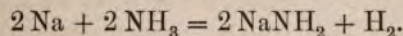
The product is **sodium amide**.   The metal amides, like the nitride of magnesium, are decomposed by water into ammonia and the hydroxide of the metal.

Ammonia combines with a number of compounds of metals, forming complex substances in some of which the metals replace part of the hydrogen in the ammonium group.

Uses. — Ammonia dissolves grease and some metallic oxides and other compounds, and is used for cleaning copper, silver, etc.   It also has many important uses both in the laboratory and in chemical industries. (*Cf.* Solvay soda process, p. 264).

Sources of Ammonia. — Ammonia is one of the products of the putrefaction of animal matter, and its salts, especially the nitrate, are found in very small amounts

in the air.   It is also produced in the decomposition of animal substances, such as horns, hides, etc., when these are heated with the exclusion of air.   The old name, "spirits of hartshorn," given to the solution of ammonia, is a reminder of this source.   Most of the ammonia and the ammonium compounds, however, are by-products of the gas and coke industries, where ammonia is formed in the destructive distillation of coal.   The ammonia and some other products are absorbed in water or dilute acids.   To purify it, the ammonia is driven off from this solution into dilute sulphuric or hydrochloric acid by heating with milk of lime.   The solution is clarified and evaporated to crystallization, and the ammonia obtained by heating the salt with slaked lime.

Ammonia is the final reduction product of nitric acid (p. 140).   As it is formed, it combines with the excess of acid to make ammonium nitrate, which remains in solution.   Evidence of the reduction which has occurred is found in the fact that, when this solution is heated with sodium hydroxide, ammonia is given off.

Detection of Ammonia. — Ammonia is readily liberated from its compounds by alkalies, as we have seen, and is detected by its odor, or by the white cloud formed when a glass rod or stopper moistened with strong hydrochloric acid is brought into it.   A far more delicate test for ammonia or ammonium salts in solution is the so-called **Nessler's reagent**, by which one part of ammonia in a billion parts of water is detected.   This test is of importance in the chemical examination of drinking water, where the presence of ammonia gives evidence that the water contains, or has contained, nitrogenous organic matter, possibly from sewage contamination.

OTHER COMPOUNDS OF NITROGEN AND HYDROGEN

Ammonia was believed for a long time to be the only compound of nitrogen and hydrogen; but two others have been obtained: **hydrazine**, N_2H_4, and **hydrazoic acid**, HN_3. **Hydrazine** is a liquid which fumes in the air and unites with water with great avidity to form a hydrate N_2H_4, H_2O, which is a strong base, forming salts like ammonia. Both hydrazine and its hydrate are strong reducing agents. Pure **hydrazoic acid** is an explosive liquid which boils at 37°. Its solution acts as a strong acid and dissolves iron, zinc, and other metals with evolution of hydrogen and formation of salts. It may be noted that the names of these substances are derived from **azote**, which is used by the French as the name of nitrogen.

Hydroxylamine, NH_2OH, can be obtained by the reduction of nitric acid under certain conditions, and by some other reactions. It is an unstable, white, crystalline substance. In solution it has an alkaline reaction, forms unstable salts by direct union with acids, such as $NH_3O.HCl$, and acts as a weak reducing agent.

The Valence of Nitrogen in its Hydrogen Compounds.— In its compounds with hydrogen alone, nitrogen is regarded as a trivalent element. This is evident in the chief hydride, ammonia. In the less stable hydrazine and hydrazoic acid, trivalent nitrogen atoms are supposed to be in partial combination with each other, and these graphic formulas represent the relations which

may exist: $H_2N{-}NH_2$, and $\begin{array}{c} N\diagdown \\ \| \quad NH. \\ N\diagup \end{array}$ In the monad

ammonium group NH^I_4 and, consequently, in the ammonium compounds, such as ammonium hydroxide, NH_4OH, and ammonium chloride, nitrogen is evidently pentavalent. In hydroxylamine, NH_2OH, the basic character indicates an hydroxyl group, and the nitrogen is trivalent, while in the salts of hydroxylamine it becomes pentavalent as in the ammonium compounds.

NITROGEN

Preparation. — We have seen that the nitrogen of the air is mixed with small amounts of the indifferent gases of the argon group; so that while atmospheric nitrogen from which the oxygen has been removed by phosphorus or copper (p. 13) may be used as nitrogen for many chemical purposes, it is not pure. Pure nitrogen can be made readily from several compounds which contain it. One common method of preparing nitrogen is by heating a strong solution of ammonium nitrite, which, as we have seen, splits up completely into nitrogen and water (p. 147). Nitrogen may also be obtained from ammonia by means of chlorine or sodium hypobromite. The reaction with chlorine has already been given (p. 145). The hydrogen chloride combines immediately with ammonia to form ammonium chloride. In carrying out this reaction it is important to keep the ammonia always in excess, otherwise the explosive nitrogen chloride will be formed. The reaction between ammonia with sodium hypobromite is:

$$2\,NH_3 + 3\,NaBrO = 3\,NaBr + 3\,H_2O + N_2.$$
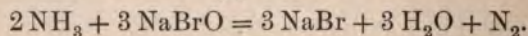
This reaction may be employed for making a volumetric analysis of ammonia.[1]

[1] "Quantitative Experiments," page 52.

Nitrogen can also be obtained from ammonia gas by means of copper oxide (p. 142), or by leading a mixture of ammonia and oxygen (or air, if pure nitrogen is not wanted) over heated copper. The action of heated iron or copper on nitrous or nitric oxide, and the decomposition of ammonium dichromate by heat, are other reactions which may be used.

Properties. — Nitrogen is without color or odor. It is a little lighter than air, a liter weighing about 1.25 grams, corresponding to the molecular weight of 28. (The discovery of argon in 1894 was due to the fact that, in a series of careful determinations of the densities of various gases, Lord Rayleigh found that atmospheric nitrogen was heavier than the nitrogen obtained from chemical compounds.) It neither burns under ordinary conditions nor does it support combustion. In these respects it is like carbon dioxide, but is distinguished from this gas by its insolubility in alkaline solutions and by not rendering limewater milky.

Nitrogen unites directly with heated magnesium and some other metals, forming nitrides. Its direct combination with oxygen and with hydrogen can be forced under certain conditions, but, in general, nitrogen is characterized by great chemical inactivity. It is, however, a constituent of many compounds, and it is on account of its chemical indifference that its compounds are so easily decomposed and therefore show such great chemical activities. The indifferent nitrogen always tends to drop out of the compound without uniting with anything else, leaving the elements with which it was combined free to enter into new combina-

tions.   The valence of nitrogen has already been discussed (pp. 140, 151).

The nitrogen of the air plays practically no part in ordinary combustions; but the passage of sparks from an induction coil through air causes a combination of nitrogen and oxygen to take place little by little (p. 131).

Nitrogen in Nature. — The discharge of atmospheric electricity in thunder storms also produces oxides of nitrogen, and the acid which results from their solution in water unites with the ammonia which is formed by the decay of organic matter, with the production of ammonium salts.   This is the origin of the ammonium salts which are found in small quantities in the air and in almost all natural waters.   The nitrogen of decaying organic matter is often oxidized through the influence of certain bacteria in the presence of bases and easily decomposed salts of basic metals, giving rise to salts containing nitrogen, such as saltpeter.   As these salts are soluble, they accumulate only when protected from the rain, as in caves, or when they are produced in rainless regions.   The vast deposits of Chile saltpeter are believed to have been formed in this way.

Nitrogen is an essential constituent of very many plant and animal substances, the animals deriving their supply of nitrogen from the vegetable substances they eat.   The plants obtain nitrogen from the ammonium and other nitrates which are formed in nature, and it was formerly supposed that this was their only natural supply; but certain leguminous plants, such as clover, peas, and beans, can assimilate the nitrogen

of the air through the action of special micro-organisms which are found in nodules on their roots. When these crops are plowed in, the fertility of the soil is increased by the presence of the micro-organisms. Cultures of this organism have been added to the soil with good effect. The nitrogen necessary for fertility is often supplied by artificial fertilizers which contain ammonium salts and nitrates. On account of the importance of nitrogen to life, methods of utilizing the atmospheric nitrogen by converting it into compounds upon which plants can feed have of late received great attention. One process, which is successfully carried out, is the union of atmospheric nitrogen and oxygen by powerful electric discharges, with the production of oxides of nitrogen; these dissolve in water, forming nitric acid, and this, in turn, with lime, gives calcium nitrate which is used as a fertilizer (Birkeland and Eyde's process). Another process makes use of nitrogen from liquid air; this is conducted over calcium carbide (p. 288) in an electric furnace, and reacts with it to form a compound which, with the moisture of the soil, produces ammonia and nitrates.

Nitrogen is sometimes used in chemical processes as an indifferent gas to displace air where the presence of oxygen would interfere with the desired reactions.

Detection of Nitrogen. — A colorless and odorless gas is usually assumed to be nitrogen, if it extinguishes flame and does not turn limewater milky. Nitrogen is detected in its compounds by converting it into ammonia or nitric acid, both of which are readily recognized. In many organic substances, the odor

of burning wool, which they give on heating, is a test
for nitrogen, and also the evolution of ammonia when
they are heated with soda lime. Where these tests
fail, nitrogen may be detected as follows: The sub-
stance is ignited with metallic sodium, and the mass is
brought into water with the addition of a little ferrous
sulphate. After warming for a short time, the solution
is made acid with hydrochloric acid, and a drop of
ferric chloride is added. If nitrogen was present, a
precipitate of prussian blue is produced (p. 341).

The Argon Gases. — In the gas which was discovered
in atmospheric nitrogen in 1894 and named argon
because of its great chemical indifference, there have
since been discovered four other gases of the same
character, helium, neon, krypton, and xenon. Helium
had been discovered some years before in the sun, by
means of the spectroscope, and is named from the
Greek word for sun. It is now known to exist in the
gases given off by certain minerals when these are
heated, and is found in some mineral springs, as well
as in the atmosphere. None of these elements form
any chemical compounds, hence they have no valence.
Physical evidence indicates that their molecules con-
tain only one atom each, so that their atomic weights
and their molecular weights found from density
determinations are the same. It is interesting to note
that the conclusion in regard to the monatomic char-
acter of the molecules is reached by a determination of
the velocity of sound in these gases.[1]

[1] Walker's "Introduction to Physical Chemistry," page 36.

CHAPTER XV

SOLUTIONS; THE IONIC THEORY; ELECTROLYSIS

SOME PROPERTIES OF SOLUTIONS

THE study of solutions has given a number of important facts.

1. When a dilute solution is cooled until crystallization occurs, the crystals are found to consist of the pure solvent, while the remaining solution becomes more concentrated. The ice which forms from salt water, for instance, is pure ice, though usually brackish from small amounts of the solution which have been mechanically inclosed in the crystals. The temperature at which the ice forms is lower than the freezing point of pure water, and the lowering of the freezing point is greater as the solution is more concentrated.

In many cases the depression of the freezing point in solutions containing equal proportions by weight of the dissolved substances is inversely proportional to their molecular weights; so that the molecular weights may be calculated from the difference between the freezing point of the solvent and that of a solution of known strength (freezing point method).

2. Solutions of non-volatile substances have a less vapor tension and consequently a higher boiling point than the pure solvent (p. 32). Here, as in the case of the freezing point, the effect is greater as the solution is stronger, and is so related to the molecular

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weight of the dissolved substance that it may be made the means for determining the molecular weight (**boiling point method**).

3. Certain membranes can be prepared which allow water to pass through them, but prevent the passage of dissolved substances. If such a " semipermeable" membrane is formed in the walls of a porous porcelain cell, and the cell, filled with a solution, is placed in pure water, the water enters the cell through the membrane, increasing the volume of the solution, or producing a pressure if the cell is closed. This pressure, which is known as **osmotic pressure,** is proportional to the strength of the solution in the cell, and is the same as the pressure which the dissolved substance would show if it occupied the volume of the solvent in the state of a gas. Osmotic pressure, in fact, follows the gas laws, not only in being proportional to the amount of substance in a given space, but also in being proportional to the absolute temperature. Further, Avogadro's hypothesis applies to dissolved substances as well as to gases. Just as equal volumes of gases at the same temperature and under the same pressure are believed to contain equal numbers of molecules, it is found that, at the same temperature, solutions of different substances which give the same osmotic pressures are those which contain equal molar weights (p. 51) of the substances, that is, equal numbers of molecules. It is obvious that molecular weights might be found from determinations of osmotic pressure as they are from gas and vapor densities.

Molecular Weights of Dissolved Substances. — The depression of the freezing point of solutions and their

osmotic pressure, as well as the elevation of the boiling point, are all related to each other and to the lowering of the vapor pressure, so that if one of these facts is known about a solution, the others can be calculated.[1] Any one of these phenomena could be used for molecular weight determinations, but in practice the measurement of vapor pressure and of osmotic pressure present experimental difficulties, so that the freezing point and boiling point methods are the ones usually employed.

Solutions of **acids, bases,** and **salts** in water show such deviations from the relations which have been described that the molecular weights of these substances cannot be found by these methods in aqueous solution; but where they are soluble in other solvents, such as benzene, chloroform, etc., the methods can be used. In aqueous solution, the classes of substances which have been named give results which indicate molecular weights that are much smaller than those which correspond to their empirical formulas, often only one half or one third as large. This suggests a dissociation of the molecules in solution, which would account for these results in the same way that the dissociation of ammonium chloride in the state of vapor was seen to be the explanation of its smaller density and a molecular weight of about half that required by its established formula. The independent behavior of the sulphate group SO_4 in sulphuric acid and all sulphates (p. 91), and of the chlorine in hydrochloric acid and all chlorides (p. 109), also points in the direction of a probable dissociation in solution. Evidence for such a dissociation is found,

[1] Walker's "Introduction to Physical Chemistry," page 175.

further, in certain phenomena which occur when an electric current is passed through such solutions.

THE IONIC THEORY

Pure water does not conduct ordinary currents of electricity, nor does the current pass through solutions of sugar or of other substances which give normal molecular weights by the methods which have just been discussed. But those substances, whose solutions lead to the smaller values which suggest dissociation, all conduct the current, and all suffer chemical change when the current passes through their solutions. Such substances are called **electrolytes,** and the chemical effect which is produced on them by the current is called **electrolysis.** The rods or plates of metal or carbon by which the electric connection is made with the solution are called **electrodes,** — that connected with the positive pole of the battery or dynamo being termed the **anode,** and that with the negative pole, the **cathode.** When a current is passed through a solution of copper sulphate, metallic copper appears at once on the cathode, no matter how far apart the electrodes may be ; and if the anode is of copper, copper is deposited on the cathode by the feeblest current. These facts and many others are explained by the **theory of ionic dissociation,** according to which all electrolytes are more or less dissociated by the act of solution into electrically charged atoms or groups, which are called **ions.** Thus, in a solution of copper sulphate there are supposed to be ions consisting of positively charged copper atoms and negatively charged sulphate groups. Since the solutions as a whole show no electric charges, the sums of the positive and

of the negative charges on the ions must be equal. In dilute sulphuric acid there are two positive hydrogen ions for each sulphate ion, and therefore the charge which the hydrogen ion carries must be half as large as that of the sulphate ion. The charge of the hydrogen ion is taken as unit charge, so that the sulphate ion must have a negative charge of two, and that of copper, a positive charge of two. In fact, the charges of the ions in hydrogen units have the same values as the valences of the atoms or groups of which the ions consist. Representing the ionic condition and the charges by the signs $+$ and $-$, the state of things in a copper sulphate and in a sulphuric acid solution may be represented thus:

$$CuSO_4 \rightleftarrows \overset{++}{Cu} + \overset{--}{SO_4};$$
$$H_2SO_4 \rightleftarrows \overset{+}{H} + \overset{+}{H} + \overset{--}{SO_4}.$$
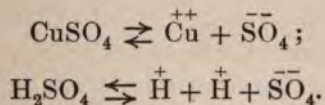
These are written as reversible reactions, since the degree of dissociation differs with the concentration. It increases with dilution and is supposed to be complete only when this is very great. When the solution is concentrated, as by evaporation, more and more ions unite, with the neutralization of their opposite electric charges, to form complete molecules, and the substance finally separates out as a solid in the molecular condition. The proportion of ions to molecules in solutions of different substances varies widely, but for any given substance it has a constant value for each concentration. The conduction of the electric current by electrolytes in solution, according to this theory, is wholly dependent on the ions which act as carriers of the current, and

M

the degree of **ionization** is determined from measurement of conductivity.

The abnormal molecular weights which electrolytes show in aqueous solution are, therefore, the consequence of the greater or less degree of dissociation of their molecules into ions. The osmotic pressure, change of the freezing and boiling points, and the lowering of vapor pressure are all phenomena which evidently depend on the relative numbers of particles in the solutions. Dissociation increases the number of these particles. Complete ionization of a binary compound such as hydrochloric acid would double the number of particles, and, as in the case of ammonium chloride vapor, would give a half value for the molecular weight. A compound which separates into three ions, such as sulphuric acid, would give one third of the normal molecular weight as the limiting value.

The difficulty of imagining copper atoms and sulphate groups as independently present in a solution of copper sulphate, or of sodium and chlorine atoms as existing in a solution of common salt, is met by the statement that the electric charges, which the ions carry, must impart properties quite different from those which the atoms or groups alone would possess. The ions may be considered as allotropic forms of the constituents of molecules, which are changed into the ordinary forms when their electric charges are lost.

ELECTROLYSIS

When the electrodes which have been placed in a solution of an electrolyte are connected with a source of electricity, they are at once charged, the anode positively

and the cathode negatively. It is a law of electrical action that bodies charged with like electricity repel each other, and bodies charged with unlike electricities attract each other. Therefore, the positively charged ions at once begin a movement towards the cathode, and the negatively charged ions towards the anode. As the ions reach the electrodes their charges are neutralized by an equal amount of the opposite kind of electricity on the electrode. In this way equal quantities of positive and of negative electricity are simultaneously lost from the anode and from the cathode, and these losses are at once made good from the battery or dynamo. Since ions are everywhere present in the solution, the products of electrolysis appear at the electrodes the instant the electric circuit is closed. This is the picture the theory gives of the conduction of the current through electrolytes.

The atoms or groups left from the discharged ions immediately unite to form molecules or enter into other reactions. For instance, in the case of sulphuric acid, the hydrogen ions which reach the cathode, on losing their charges, become hydrogen atoms which at once form hydrogen molecules and escape as gas ; while the SO_4 groups, left from the discharge of the sulphate ions at the anode, react with the water with which they find themselves in contact to form sulphuric acid and oxygen: $SO_4 + H_2O = H_2SO_4 + O$, and the oxygen atoms unite and escape as oxygen gas. The hydrogen and oxygen produced by this electrolysis are evolved in the proportion in which these gases unite to form water, and in the end it is water alone which has disappeared from the solution, so that this experiment is often made

as a volumetric analysis of water. But in making the experiment it should be understood that the electrolyte plays an important part.

In the electrolysis of a solution of sodium hydroxide, oxygen and hydrogen are again given off in the proportion in which they form water, and water alone is removed from the solution. But here, as with sulphuric acid, it is the dissolved substance and not the water which is first affected. The ions of sodium hydroxide are sodium ions $\overset{+}{N}a$, and hydroxyl ions $\overset{-}{O}H$:

$$NaOH \rightleftarrows \overset{+}{N}a + \overset{-}{O}H.$$
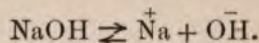
When the sodium ions are discharged at the cathode, the sodium reacts with water to form sodium hydroxide and hydrogen, and the hydroxyl groups set free at the anode react with the production of water and oxygen:

$$\overset{+}{N}a + \overset{-}{O}H \rightleftarrows NaOH;$$

$$2\overset{-}{O}H = H_2O + O.$$
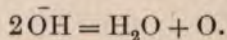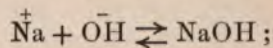
With copper sulphate solution, copper is deposited on the cathode and oxygen set free at the anode as in the electrolysis of sulphuric acid.

Since the supply of electricity from the battery or dynamo is utilized, according to this theory, simply to neutralize the charges of the discharging ions, the amount of electric current used in electrolysis must be proportional to the number of unit charges which disappear from the ions. Hence the same quantity of electricity or the same current passing through different solutions for the same time, should cause the separation

of chemically equivalent amounts of substances. Thus, the amount of electricity which would cause the evolution of 1 gram of hydrogen ($H = 1$) should set free 23 grams of sodium ($Na = 23$), 35.46 grams of chlorine ($Cl = 35.46$), 8 grams of oxygen ($O = 16$), or deposit 31.78 grams of copper ($Cu = 63.57$), or 107.88 grams of silver ($Ag = 107.88$).

This is, in fact, the case, and was an established law of electrolysis long before the theory took its present form. **Faraday's laws of electrolysis** state that : 1. *The amount of any one substance which is liberated in a given time is proportional to the strength of the current;* and 2. *The amounts of different substances which are liberated by the same current in equal times are proportional to their chemical equivalents.*

The theory of ionic dissociation serves to explain the fact that the same amount of heat is developed by the neutralization of equivalent quantities of strong acids by strong bases. For when the acid and the base are brought together, the one thing that happens in all cases is the formation of an equivalent amount of water from the discharge and union of hydrogen ions of the acid and hydroxyl ions of the base, the other ions being unaffected :

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = H_2O + \overset{+}{Na} + \overset{-}{Cl}.$$
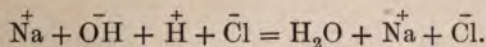
In general, chemical reactions in solutions are considered to be reactions between ions. When ions can combine to form insoluble substances or gases which can escape from the solution, they unite in these ways with the neutralization and disappearance of their electrical charges. The degree of chemical activity

of a dissolved substance is considered to be an expression of the degree to which it is dissociated into ions. According to this theory, acids owe their acidity to the presence of hydrogen ions, and alkalies their alkalinity to the presence of the hydroxyl ions. The definitions of acid and base, therefore, take these forms: an acid is a compound whose solutions contain hydrogen ions; a base is a compound whose solutions contain hydroxyl ions.

The following equations are given as further illustrations of the way in which ionic reactions may be expressed. The dot represents a unit positive charge and the dash a unit negative charge:

$$Zn + H\cdot + H\cdot + SO''_4 = Zn\cdot\cdot + SO''_4 + H_2.$$
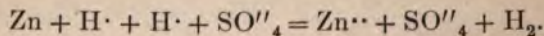
Here the two hydrogen ions give up their charges to zinc, which thus becomes a zinc ion, while hydrogen escapes as gas.

$$H\cdot + H\cdot + SO''_4 + Ba\cdot\cdot + Cl' + Cl' =$$
$$BaSO_4 + H\cdot + H\cdot + Cl' + Cl'.$$
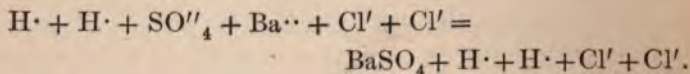
In this case the only change which occurs is that the charges of the barium and of the sulphate ions neutralize each other and molecular barium sulphate is precipitated.

In ordinary solutions of acids, bases, and salts, in which only part of the molecules are dissociated, further separation into ions takes place as the existing ions disappear in reaction, until, in such reactions as those just given, almost all of the reacting ions have been converted into molecular compounds. In reversible reactions, equilibrium is of course reached before this occurs.

CHAPTER XVI

CARBON

CHARCOAL has been used in some experiments as a form of the elementary substance **carbon**. When burned in air or in oxygen it gives the gas called carbon dioxide, which extinguishes flame and renders limewater milky. Whenever this gas appears in a chemical reaction, we may infer that carbon was present in the reacting substances. Most plant and animal substances not only produce carbon dioxide when burned, but char when heated, or burn with a sooty flame; and the appearance of a black char or of soot, which can afterwards be burned, is sufficient evidence of the presence of carbon. Some volatile substances, however, which contain carbon, like alcohol and kerosene, leave no residue when heated, and often give no soot when burned. Some minerals, too, fail to give this test, but evolve carbon dioxide when treated with acids. The production of carbon dioxide from a substance is, therefore, the final and characteristic test for the presence of carbon.

Occurrence of Carbon. — By these tests it is found that carbon is a constituent of a very large number of natural substances. It is contained in most substances found in living organisms and in those derived from them; in coal, petroleum, and natural gas; and in limestone and other minerals. Carbon also occurs almost pure as

graphite and as diamond. In the so-called "organic" substances of natural origin, carbon is combined chiefly with hydrogen, forming hydrocarbons, or with hydrogen and oxygen, as in sugar and the carbohydrates. In some important plant and animal tissues, besides these elements, nitrogen, and, to a less extent, phosphorus and sulphur are found. In the minerals which contain carbon, this element is in combination with oxygen and metals in the form of carbonates. Carbon dioxide is, as we know, a constant component of the air, from the combustion of fuels, and from the slow oxidation processes of respiration and of the decay of organic substances.

Besides these natural compounds of carbon and those immediately derived from them, such as alcohol, acetic acid, glycerine, etc., a vast number of compounds of carbon have been made in the laboratory. The number of carbon compounds is so great — over 100,000 — and they show such peculiarities in their relationships and properties, that a separate branch of chemistry is devoted to their study. This is called **Organic Chemistry, or the Chemistry of the Compounds of Carbon.** While organic chemistry, under the definition just given, properly includes the study of all the compounds of carbon, the element itself and a few of its compounds are so closely related to inorganic substances that they are always described in inorganic chemistry.

Varieties of Carbon. — Pure carbon burns completely to carbon dioxide and gives no other product. Tried by this test, only two natural substances are found which are nearly pure carbon. These are graphite and the diamond.

Graphite is a grayish, lustrous substance, soapy to the touch and very soft. It is usually intimately mixed with mineral substances and is in this sense impure. It is crystalline, though well-formed crystals are seldom found. The "leads" of pencils are made of graphite mixed with fine clay. Under the name of "black lead," or "plumbago," it is used as a protective coating for iron and as a lubricant for machinery. It withstands high temperatures and is unaffected by most chemical agents, and is employed on these accounts for making graphite crucibles. It is a good conductor of electricity and is used to coat molds for electrotyping. Artificial graphite is made from anthracite or coke by the intense heat of the electric furnace, and the product is especially adapted for the electrodes used in batteries, for electrolysis, and for the arc light.

Diamond. — The form of carbon known as the diamond is also crystalline, and occurs in many varieties from the transparent, colorless, or slightly tinted diamonds used as gems, to the black, opaque, and impure carbonadoes which are employed as drills for rock. The specific gravity of the diamond is about one and a half times that of graphite. It is rather brittle and is the hardest substance known. The natural diamonds are irregular in shape and often covered with an opaque crust. For use as gems they are cut, or rather ground, by the aid of diamond powder, to various geometric forms which have no relation to the natural crystalline form, and which are chosen for the purpose of gaining the most brilliant effects. The brilliancy of a skillfully cut stone depends on the very high refractive index of the diamond, which occasions an unusual amount of "total reflection" from

the interior surfaces. The play of colors is due to the dispersion which always accompanies refraction.

Artificial diamonds have been made, though only of microscopic size, by causing carbon dissolved in molten iron to separate under enormous pressure. Molten iron tends to expand when it becomes solid. Consequently, when a mass of molten iron saturated with carbon is plunged into water, the unyielding crust which is formed compels the slowly cooling liquid within to exert a tremendous pressure. Under these conditions some of the carbon assumes the crystalline form of diamond.

All diamonds contain foreign substances; the colorless diamonds usually mere traces, while the carbonadoes sometimes have as much as 5 per cent of ash.

Amorphous Carbon. — All forms of carbon, natural and artificial, except the diamond and graphite, are without crystalline form, or **amorphous**. The coals, which occur in great variety, are the remains of prehistoric vegetable growths which have been gradually changed by natural causes into a mixture of carbon and compounds richer in carbon than the original material. The change has been most complete in the anthracite, less in the bituminous coals, and least in the lignite and peat.

Coke. — When coal is heated without access of air, further decomposition occurs and a residue is obtained which, besides the ash, contains an amount of carbon varying from 30 to 90 per cent of the original weight of the coal. This residue is called coke. It is employed as a fuel for producing high temperatures, and in metallurgy as a reducing agent, having an advantage over coal for this purpose, because the sulphur which is con-

tained in the coal in the form of pyrites is driven off in the coking process.

Charcoal is produced when solid organic substances are incompletely burned or are heated out of the air. Wood charcoal is made by partly burning wood which has been piled in great heaps and covered with sod, openings to the air being left so that the wood smolders until the change is completed. About 20 per cent of the weight of the wood is obtained as charcoal. A more economical method is that of heating the wood in closed retorts (**destructive distillation**). This gives a yield of about 30 per cent, and the gases and tar are utilized. Charcoal retains the form and the structure of the wood with about three quarters of its bulk. It is used in making black gunpowder and for the production of certain high grade steels, as it contains little or no sulphur or phosphorus. **Animal Charcoal** or **Bone Black** is the residue from the destructive distillation of bones. It contains all the inorganic matter of the bones, chiefly calcium phosphate, with 15 or 20 per cent of carbon from the organic matter. Both wood and animal charcoal are very porous and have the property of absorbing gases and withdrawing coloring matters and other dissolved substances from their solutions. Animal charcoal is the more efficient in this latter respect, and is used to decolorize sugar solutions before their crystallization, and also to clarify glycerine, oils, etc. Charcoal is also used to remove objectionable gases from the air, and as a filter for drinking water. The efficiency of the charcoal used for these purposes may be restored by heating; but after repeated employment, the pores become choked from the carbonization of the

organic matters which have been absorbed. In this case animal charcoal is burned to bone ash which is converted into superphosphate for fertilizing (p. 287).

Lampblack is the finely divided form of carbon given off as black smoke or soot when oily and resinous substances are burned. It is used as a pigment in paints, printer's ink, and India ink.

Gas Carbon is an exceedingly hard, dense form of nearly pure carbon, which is deposited at the outlet of the retorts in making gas from coal. It is a good conductor of electricity, and before the manufacture of artificial graphite was used for electrodes.

All these varieties of carbon, except gas carbon, contain small amounts of hydrogen and oxygen compounds of carbon. For laboratory purposes pure carbon is usually made from sugar, the charred residue being heated to a high temperature in a covered crucible.

General Properties. — At the temperature of the electric furnace all other varieties of carbon are converted into graphite, and in the electric arc, carbon slowly volatilizes and thus limits the maximum temperature of the arc (3500°). All forms of carbon are insoluble in ordinary solvents, but dissolve in iron and a number of other metals when these are melted, separating as graphite when the metal cools, or remaining wholly or partly in combination as a metallic carbide. At very high temperatures, carbon unites directly with boron, silicon, and several metals to form carbides, and with hydrogen to form acetylene. Amorphous carbon at a red heat combines with sulphur vapor with the production of carbon disulphide.

The temperature at which union with oxygen be-

gins varies with the form of the carbon. The diamond, graphite, and the denser kinds of amorphous carbon require a red heat, while lampblack and charcoal kindle much more readily. Wood charcoal, powdered immediately after its preparation, sometimes take fire spontaneously, a danger which has to be guarded against by the makers of gunpowder.

Carbon almost invariably acts as a tetravalent element; only in carbonic oxide and a few organic compounds is it divalent.

CARBON DIOXIDE

The quantitative composition of this compound of carbon and oxygen has been determined by burning a known weight of pure carbon and absorbing the gas in a solution of potassium hydroxide. The increase in weight of the solution gives the weight of the carbon dioxide. In this way it is found that one gram of carbon unites with 2.667 grams of oxygen to produce 3.667 grams of carbon dioxide. From these figures the empirical formula CO_2 is derived in the usual way; and as the density of the gas is found [1] to be 1.53 (air $= 1$), this is also the molecular formula.

Occurrence and Preparation. — Although the proportion of carbon dioxide in the air is so small, the total amount is enormous. It is calculated that the atmosphere contains 4.7 kilograms of this gas for every square meter of the earth's surface, and that, consequently, the amount in the whole atmosphere is about 2450 thousand million tons. This corresponds to about 670 thousand million tons of carbon, so that carbon dioxide

[1] "Quantitative Experiments," page 36. See also page 56.

is probably the most abundant compound of carbon. Carbon dioxide issues from the ground in volcanic districts in large amounts, two notable localities being the Valley of Death in Java, and the Grotto del Cane near Naples. On account of its weight, the gas diffuses slowly, and unused pits and caves should be tested by a burning light before one ventures into them. Carbon dioxide is also found in many mineral spring waters, such as those at Saratoga, Selters, and Vichy, where it is dissolved under pressure, and escapes with effervescence when the water comes into the air.

Carbon dioxide is produced as the final oxidation product of carbon and of all organic substances. It is not only formed when such substances are burned in an excess of air or oxygen, but is also a product of the milder oxidations which take place in respiration, and in fermentation and decay. It is usually prepared for laboratory purposes by the action of dilute hydrochloric acid on marble or other carbonates, and on account of its solubility in water is collected by displacement of air or over mercury. It may also be obtained from most carbonates by heating them, and is often prepared for industrial purposes by heating limestone, as well as by the combustion of charcoal or coke. In the latter case the gas is, of course, diluted with the nitrogen of the air. The carbon dioxide from volcanic sources, from mineral springs, and that which results from the fermentation in breweries, is also sometimes utilized. Carbon dioxide was the first gas which was distinguished from air (Von Helmont, 1644).

Properties. — Carbon dioxide has no color or odor. Its critical temperature is 31.1°. The liquid is sold in

steel cylinders for making "soda water," etc., and for
some other purposes. Liquid carbon dioxide boils at
$-79°$. When it is allowed to escape from a jet into the
folds of a dry cloth, so much cold is produced by rapid
evaporation, that part of it is converted into a white,
snow-like mass which slowly evaporates without melt-
ing. Mixed with ether the solid may be used to cool
substances to $-80°$.

Carbon dioxide dissolves in its own volume of water
whatever the pressure, so that the actual amount or
weight of gas dissolved is proportional to the pressure;
and when the pressure is released, as in drawing soda
water or uncorking a bottle in which the gas has been
generated by fermentation, part of it escapes.

Carbon dioxide is a stable compound, and only partly
decomposed at very high temperatures. It extinguishes
most flames, but burning magnesium ribbon continues
to burn in the gas with the formation of magnesium
oxide and liberation of carbon :

$$CO_2 + 2\ Mg = 2\ MgO + C.$$
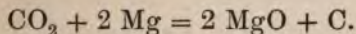
Sodium and potassium act in a similar manner, but with
the production of carbonates of the metals:

$$3\ CO_2 + 4\ Na = 2\ Na_2CO_3 + C.$$
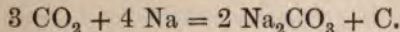
Other less active metals, such as zinc, when heated in a
current of the gas, reduce it only to carbon monoxide :

$$CO_2 + Zn = ZnO + CO.$$
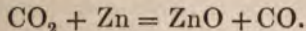
Carbon dioxide unites directly with some oxides of metals
with the formation of carbonates. This is illustrated in

its action on sodium, given above, where we must suppose that sodium oxide is first formed; and also by its union with lime :

$$CaO + CO_2 = CaCO_3.$$
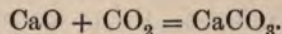
Relation of Carbon Dioxide to Life. — In the respiration of animals the oxygen from the air which is inhaled brings about a slow oxidation of the tissues, and the heat of this chemical process maintains the temperature of the body.   The carbon dioxide which is produced finds its way to the lungs and is exhaled.   Plants also take up oxygen and give off carbon dioxide.   But in sunlight the green chlorophyll causes an opposite reaction in which carbon dioxide is decomposed, and part of its oxygen set free in the air, while the carbon, the remaining oxygen, and water are gradually synthesized into starch, sugar, etc.   This reaction goes on in the daytime far more rapidly than the opposite reaction.   It is an endothermic reaction and the energy necessary for its occurrence is supplied by the sun's rays.   All of the complicated substances of the plant organism, the proteins, carbohydrates, fats, resins, organic acids, etc., are produced from a few simple substances such as carbon dioxide, water, ammonia compounds, and nitrates. When vegetable substances are used for food, or are burned, or suffer decomposition through fermentation or decay, the solar energy which has thus been stored in them is more or less completely set free.   In general, it may be said that the chemical reactions which attend plant life are synthetic and endothermic, while in animals they are analytic and exothermic.

Carbon dioxide is not directly poisonous, but when

present in air in considerable quantity may cause death by preventing a sufficient supply of oxygen, as would be the case with any indifferent gas, such as nitrogen. Various exhalations which accompany the discharge of carbon dioxide from the lungs, however, appear to be harmful, and their presence as well as that of an undue proportion of carbon dioxide must be avoided by ventilation. The determination of the amount of carbon dioxide is used as an index of the quality of the air in audience halls, etc.

Carbonic Acid and Carbonates. —The solution of carbon dioxide in water is weakly acid. Although the gas can be entirely driven out of its solution by boiling, we have the same reason for assuming that an unstable carbonic acid is present in the solution, as we had for the existence of sulphurous acid in solutions of sulphur dioxide, since many stable **carbonates** are known which correspond to an acid of the formula H_2CO_3. Carbon dioxide is, therefore, an **acid anhydride**, and the acid is formed by its union with water in the strongly reversible reaction :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3.$$
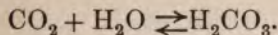
Most carbonates are decomposed by heat :

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$
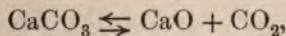
and all carbonates are decomposed by acids, even by dilute and weak acids, such as acetic acid, with the formation of carbonic acid which at once breaks up into water and carbon dioxide :

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

N
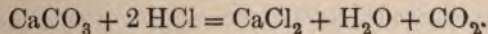
Besides the normal carbonates, such as $CaCO_3$ and Na_2CO_3, there are acid carbonates, such as $NaHCO_3$. The acid carbonate of calcium, $CaH_2(CO_3)_2$, or $Ca(HCO_3)_2$, is soluble, and is the chief occasion of the "temporary hardness" of natural waters (p. 282). Many basic carbonates are also known, an important one being "white lead," which is used for paint.

Since carbon dioxide is an acid anhydride, it is absorbed freely by solutions of bases with the formation of salts.   This fact is employed for determining the weight of the gas given off in a chemical reaction (*cf.* p. 81) :

$$CO_2 + NaOH = NaHCO_3.$$
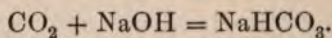
CARBON MONOXIDE

Composition and Formula. — When carbon dioxide is led through a tube containing heated zinc dust, the zinc is oxidized and a gas formed, which is insoluble in water and in alkalies, and which burns with a pale blue flame to carbon dioxide.   This gas is obviously a lower oxide of carbon which may have the formula CO, though other formulas such as C_2O_3 would be possible.   On determining the density of the gas,[1] we find that it is about 0.697 (air $= 1$), or that a liter weighs 1.25 grams. This gives a molecular weight of 28, which agrees with the formula CO.   Further, if the experiment with the zinc dust and carbon dioxide is carried out quantitatively,[2] it is found that for a gain in weight of the zinc of one gram (oxygen), the weight of the gas which is collected (found from its normal volume and density) is about 1.75 grams.   That is, from 2.75

[1] "Quantitative Experiments," page 36.   [2] *Ibid.*, page 56.

grams of carbon dioxide 1.75 grams of the gas have been produced. This leads to the formula CO; for $2.75 : 1.75 : : 44$ (CO_2) : 28. The equation for the reaction has already been given (p. 175).

Preparation. — Carbon monoxide may be prepared by the reaction we have studied, and can also be made in several other ways. It is frequently prepared in the laboratory by heating oxalic acid with concentrated sulphuric acid :

$$C_2H_2O_4 - H_2O = CO_2 + CO.$$
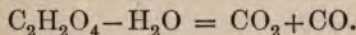
The sulphuric acid simply withdraws the elements of water from the oxalic acid, as it does from so many organic substances (p. 86). To obtain the pure monoxide, the dioxide produced with it is absorbed by passing the gases through a strong solution of sodium or potassium hydroxide.

Carbon monoxide is also formed in a number of other reactions. When carbon dioxide passes over red-hot carbon, it is reduced :

$$CO_2 + C = 2CO.$$
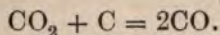
In this way the monoxide is produced in most coal fires, where the dioxide first formed at the bottom of the fire has to pass through the glowing coal above. Its presence is shown by the bluish flame which plays over the surface of the fire. Carbon monoxide is also a product of the action of heated carbon on metallic oxides or on carbonates :

$$ZnO + C = Zn + CO ;$$

$$CaCO_3 + C = CaO + 2CO.$$
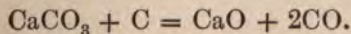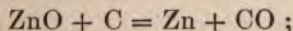
Properties. — Carbon monoxide is a colorless, odorless, and tasteless gas. It is very poisonous, forming a compound with the hæmoglobin of the blood, which is much more stable than that which is formed by oxygen, and thus renders the normal reaction with oxygen impossible. The toxic effect is produced by very small amounts of the gas.

Carbon monoxide is a good reducing agent at a high temperature, being itself oxidized to the dioxide. It plays an important part in the reduction of iron from its oxide in the blast furnace :

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2.$$
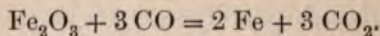
It unites directly with chlorine, forming **carbonyl chloride**, $COCl_2$, which is a gas above 8°. This compound reacts at once with water forming hydrochloric and carbonic acids :

$$COCl_2 + 2\,H_2O = 2\,HCl + H_2CO_3.$$
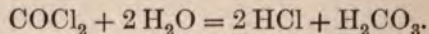
Carbon monoxide also unites directly with some metals, and attempts have been made to employ the volatile nickel compound $Ni(CO)_4$ in the extraction of this metal. The gas is absorbed by solutions of cuprous chloride in ammonia or in hydrochloric acid; but there is no simple test by which small amounts of it can be detected in the air.

FUEL GASES

Carbon monoxide is an essential constituent of gases which are extensively used as fuel in industrial operations.

Water Gas is made by blowing steam over white-hot anthracite or coke. It is principally a mixture of carbon monoxide and hydrogen:

$$C + H_2O = CO + H_2.$$
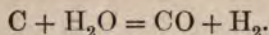
From this equation we see that 12 grams of carbon and 18 grams of steam give 28 grams of carbon monoxide and 2 grams of hydrogen. This reaction proceeds with absorption of heat — is endothermic — for, though the union of 12 grams of carbon with 16 grams of oxygen to form carbon monoxide produces about 29,000 calories, the decomposition of 18 grams of water requires about 58,000 calories ; so that for the making of 28 grams of carbon monoxide and 2 grams of hydrogen, the difference, or 29,000 calories, must be supplied. The coal or coke is first brought to incandescence by a blast of air, and then steam is substituted for the air. The temperature falls on account of the endothermic character of the reaction, and at a temperature below 1000° carbon dioxide instead of the monoxide begins to be formed :

$$C + 2 H_2O = CO_2 + 2 H_2.$$
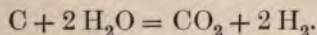
When the temperature has fallen to this point, therefore, the steam is shut off, and the air blast turned on again to raise the temperature.

When the gas is used as a fuel gas, the gases produced by the air blast are saved, but when it is employed for making illuminating gas these usually go to waste. As water gas burns with an almost colorless flame, it is " enriched " with naphtha or oil gas for illuminating purposes.

Producer Gas is a fuel gas obtained by forcing air, and often superheated steam, through a bed of incandescent coal or coke in a furnace of special design. The air alone gives a mixture of 28 to 30 per cent of carbon monoxide with about 60 per cent of nitrogen and some carbon dioxide. The steam produces water gas, and this increases the fuel value. Producer gas is used in connection with a system of **regenerative heating.** In the regenerative furnace the hot gases of combustion are employed to heat the producer gas and the air which are fed to the furnace, with the result that much higher temperatures are obtained than would be possible without this preliminary heating.

The heat of combustion of 12 grams of carbon to carbon dioxide is 96,000 calories, which is about three times that produced in the formation of the monoxide. Carbon monoxide, therefore, has about two thirds of the fuel value of the carbon from which it is made. The mixtures of carbon monoxide and hydrogen in water gas, if used hot, should theoretically give the same amount of heat as the coke from which they are made. In practice, about 92 per cent of this heat is obtained, and the convenience of the gaseous fuel, and the control of temperature which it permits, more than make up for this loss and the other costs of its production, such as the fuel necessary to maintain the temperature required for the reaction.

SOME OTHER COMPOUNDS OF CARBON

Carbon Disulphide, CS_2, is made by passing sulphur vapor over glowing charcoal or coke. It is a strongly refracting liquid which boils at 46°. It is insoluble in water. The pure substance is colorless and without ob-

C + H₂ O + O₂ → 2 C O
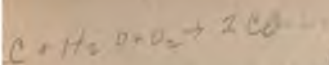
jectionable odor, but the commercial product is usually slightly yellow and has a very offensive odor due to impurities.   It is an excellent solvent for sulphur, phosphorus, iodine, fats, oils, and rubber, and is used industrially for extracting fats and oils and for vulcanizing rubber.   Its vapors are inflammable and poisonous.

Carbon Tetrachloride, CCl_4, is also a good solvent for many substances which do not dissolve in water. It is a liquid boiling at 76°.   It is not inflammable, and is less poisonous than the disulphide.   It is made by leading carbon disulphide vapor and chlorine through red-hot porcelain tubes, or by passing chlorine into the liquid disulphide in which a little iodine is dissolved. The iodine acts as a contact agent :

$$CS_2 + 3\ Cl_2 = CCl_4 + S_2Cl_2.$$
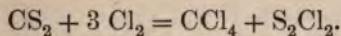
Cyanogen and Hydrocyanic Acid. — Although carbon and nitrogen do not combine with each other under ordinary conditions, a compound of the two elements can be made indirectly.   When organic compounds containing nitrogen are heated with sodium or potassium, a soluble substance is formed which contains carbon and nitrogen united with the metal, in the proportions which are expressed in the formula KCN. When this compound is treated with an acid, and the mixture distilled, **hydrocyanic acid**, HCN, is obtained, which contains the cyanogen group CN as an acid radical.   This acid, which is also known as "prussic acid," can be prepared as an anhydrous liquid which boils at 26°.   It has a characteristic odor resembling that of bitter almonds, and is exceedingly poisonous. It mixes in every proportion with water, and is a very

weak acid, being only slightly ionized in solution.   It tends to decompose in solution, and strong acids or alkalies convert it into ammonia and formic acid :

$$HCN + 2 H_2O = NH_3 + H.CO.OH.$$
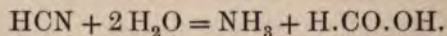
With an acid the ammonium salt is formed; with an alkali the alkaline formate is produced.   Both the anhydrous acid and its strong solutions are inflammable and burn with a violet flame.   Its salts, the **cyanides**, are decomposed even by carbonic acid, so that potassium cyanide smells of the acid in moist air.   Potassium cyanide is a valuable reagent in the laboratory, and both it and the sodium cyanide are used in the extraction of gold.

Mercuric cyanide, $Hg(CN)_2$, is made by the action of the acid on mercuric oxide, and when heated to redness gives off a colorless gas which is **cyanogen** :

$$Hg(CN)_2 = Hg + (CN)_2.$$
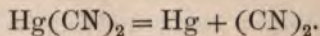
Cyanogen is most readily prepared by gradually adding a strong solution of potassium cyanide to a solution of copper sulphate and warming.   Cupric cyanide, $Cu(CN)_2$, is first formed and then breaks down into cuprous cyanide, $Cu(CN)$, and cyanogen.

Cyanogen is a colorless gas with a peculiar odor, and burns with a purple-fringed flame.   It is poisonous. The name of cyanogen was given to the group because of its presence in the blue compound known as "prussian blue."

CHAPTER XVII

SOME ORGANIC COMPOUNDS

CARBON is unique among the elements in the very great number of compounds which it forms. The study of these compounds shows that this is due largely to the exceptional power of the carbon atoms of uniting with each other with part of their valences. In this way chains or rings of carbon atoms are formed with which other elements or groups are combined. The study of organic chemistry is greatly aided by the fact that large groups of closely related compounds exist, so that the behavior of each group may be characterized in a general statement. In order to obtain a clear understanding of these compounds the use of constitutional and graphic formulas is indispensable.

THE HYDROCARBONS

Some 250 compounds of carbon and hydrogen alone are known. The simplest of these is methane, CH_4. This is the first member of an **homologous series**, each of whose members differs from those which stand next it by CH_2. It is possible to write a general formula C_nH_{2n+2} which represents any member of the series. This is known as the **paraffine series**. The first four members are: methane, CH_4, ethane, C_2H_6, propane, C_3H_8, and butane, C_4H_{10}. The graphic formulas are:

185

$$
\begin{array}{cccc}
\mathrm{H} & \mathrm{H\ \ H} & \mathrm{H\ \ H\ \ H} & \mathrm{H\ \ H\ \ H\ \ H} \\
| & |\ \ | & |\ \ |\ \ | & |\ \ |\ \ |\ \ | \\
\mathrm{H-C-H,} & \mathrm{H-C-C-H,} & \mathrm{H-C-C-C-H,} & \mathrm{H-C-C-C-C-H.} \\
| & |\ \ | & |\ \ |\ \ | & |\ \ |\ \ |\ \ | \\
\mathrm{H} & \mathrm{H\ \ H} & \mathrm{H\ \ H\ \ H} & \mathrm{H\ \ H\ \ H\ \ H} \\
\text{Methane} & \text{Ethane} & \text{Propane} & \text{Butane}
\end{array}
$$
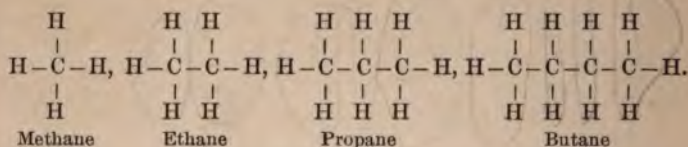
All of the members of this series up to $C_{24}H_{50}$, and a few others, are known. From butane up, other compounds of the same empirical formula are possible and a number of them have been prepared. Although they have the same percentage composition and the same molecular weight, the physical and chemical behavior of these compounds is different. They are termed **isomeric compounds**, and their differences are expressed by different relations of the atoms to each other in the graphic formulas. Thus there are two butanes, whose difference is expressed in the formulas:

$$
CH_3-CH_2-CH_2-CH_3 \text{ and } \frac{CH_3}{CH_3}{>}CH-CH_3,
$$
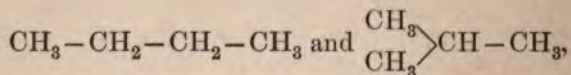
in which the groups of carbon and hydrogen atoms are written in more compact form than in the first formulas. While there are only two isomeric butanes, the number of possible isomers rapidly increases in the higher members of the series, and no less than eighteen of the formula C_8H_{18} can, theoretically, be made. This principle of isomerism runs through all organic chemistry.

A large number of the paraffine series occur in nature, especially in petroleum. **Methane** is produced by the decomposition of organic matter under certain conditions, and is contained in the bubbles of gas which are disengaged when the bottom of marshy pools is disturbed. On this account it is called " marsh

gas." It also issues from seams in coal mines and is there called "fire-damp," which mixing with air gives rise to disastrous explosions. Methane is a light gas which burns with an almost colorless flame.

The first four members of this paraffine series are gases. From C_5H_{12} to $C_{15}H_{32}$ they are liquids and the rest are solids. They are all insoluble, or nearly so, in water, and all are characterized by great indifference to most chemical reagents. Chlorine, however, acts on some of them in sunlight and on others when heated, producing compounds in which chlorine is substituted for hydrogen. Among these substitution products of methane is **chloroform**, $CHCl_3$, which is usually made, however, in another way. An analogous compound, **iodoform**, CHI_3, is used as an antiseptic in surgery. When heated with exclusion of air, the paraffines tend to break up into hydrogen and compounds with a greater proportion of carbon, and may even give carbon itself.

Besides the paraffine series of hydrocarbons there are several others whose members have the same successive difference in composition. In the **ethylene series** the general formula is C_nH_{2n}. The first member of this series is ethylene, C_2H_4, a gas which burns with a luminous flame. Acetylene, C_2H_2, is the first member of the **acetylene series**, whose general formula is C_nH_{2n-2}. In both the acetylene and ethylene series the members unite directly with hydrogen or with chlorine, and are on this account called "unsaturated" compounds. This behavior is explained by the fact that the hydrogen in these compounds is insufficient to satisfy the carbon valences.

Acetylene is produced when an electric arc between

carbon rods is formed in hydrogen. It is commonly prepared by the action of water on calcium carbide:

$$CaC_2 + 2 H_2O = Ca(OH)_2 + C_2H_2.$$
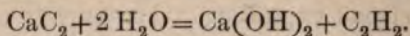
Acetylene burns from an ordinary jet in a smoky flame, and when used for illuminating purposes special burners are employed. The flame is then small but very bright. The gas is an endothermic compound and at pressures of more than two atmospheres is readily exploded:

$$C_2H_2 = 2C + H_2(+53,200 \text{ calories}).$$
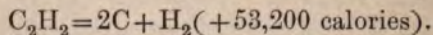
One other series of hydrocarbons is of great importance. This is the **benzene series**, whose first member is benzene, C_6H_6, and whose general formula is C_nH_{2n-6}. Benzene and other hydrocarbons of this series are among the products obtained by the destructive distillation of coal in making illuminating gas. The behavior of benzene is accounted for by giving it a formula in which the carbon atoms are united in a closed ring. The greater number of carbon compounds are derived from benzene.

DERIVATIVES OF THE HYDROCARBONS

All of the other organic compounds may be regarded, theoretically, as derivatives of the hydrocarbons, though they are not usually made from them.

Alcohols. — The alcohols are compounds in which one or more hydrogen atoms of a hydrocarbon are replaced by the hydroxyl group. **Methyl alcohol**, which is also known as "wood alcohol" because it is a product of the destructive distillation of wood, has the formula CH_3OH, in which one hydrogen atom of methane is replaced by hydroxyl, and **ethyl alcohol**, $CH_3 - CH_2OH$,

which is ordinary alcohol, bears a similar relation to ethane CH_3-CH_3. **Glycerine** is another alcohol containing three hydroxyl groups $CH_2OH-CHOH-CH_2OH$, and is related to propane $CH_3-CH_2-CH_3$.

The alcohols have basic characteristics, their hydroxyl groups being replaceable by acid radicals:

$$CH_3OH + HCl = CH_3Cl + H_2O.$$
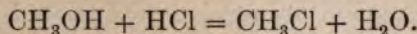
Ethers. — The ethers stand in a relation to the alcohols that oxides of metals do to the hydroxides. **Ordinary ether** $(CH_3-CH_2)_2O$ is made by the action of sulphuric acid on alcohol with the withdrawal of the elements of water, $2\,C_2H_5OH - H_2O = (C_2H_5)_2O$, and is commonly called sulphuric ether on this account.

Aldehydes. — By the careful action of oxidizing agents on alcohols there is formed, first, an aldehyde which in composition is equal to the alcohol less two atoms of hydrogen. The aldehydes $HCO.H$ and $CH_3CO.H$ stand in this relation to methyl and ethyl alcohols. The monad group $CO.H$ is characteristic of an aldehyde. **Formaldehyde**, $HCO.H$, is largely used as a disinfectant and is sold in a 40 per cent solution under the name of "formaline." The aldehydes are good reducing agents, being readily oxidized to acids.

Acids. — On further oxidation of alcohols, or by the oxidation of aldehydes, organic acids are formed. The successive production of an aldehyde and an acid from an alcohol is shown by the following equations:

$$CH_3CH_2OH + O = CH_3CO.H + H_2O;$$

Alcohol　　　　　　　Aldehyde

$$CH_3CO.H + O = CH_3CO.OH.$$

Aldehyde　　　　　　Acid
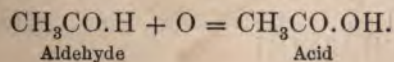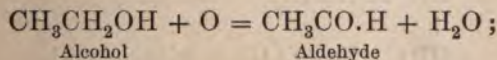
The group CO.OH, called the carboxyl group, is contained in all organic acids. The hydrogen of this group only can be replaced by metals in the formation of organic salts.

Acetic acid, $CH_3CO.OH$, is one of the products of the destructive distillation of wood, and is also made by the oxidation of dilute alcohol with the aid of certain bacteria, "mother of vinegar." The dilute acid is known as vinegar. **Oxalic acid** is a solid which crystallizes as the hydrate $\begin{vmatrix} CO.OH \\ \\ CO.OH \end{vmatrix}$, $2\,H_2O$. It is a dibasic acid. When heated it breaks up into carbon dioxide and **formic acid :**

$$(CO.OH)_2 = CO_2 + H.CO.OH,$$
$$\text{Oxalic acid} \qquad\qquad \text{Formic acid}$$
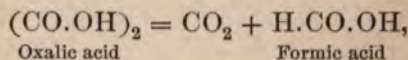
and the formic acid is partly decomposed into water and carbon monoxide. With concentrated sulphuric acid, oxalic acid gives water and the two oxides of carbon (p. 179). It is readily oxidized in solution and acts as a good reducing agent, being employed for this purpose in analytical chemistry.

Among the other well-known organic acids are **tartaric** acid $\begin{vmatrix} CH(OH)-CO.OH \\ \\ CH(OH)-CO.OH \end{vmatrix}$, a dibasic acid, and **citric acid** (the acid of lemons) :

$$\begin{matrix} CH_2CO.OH \\ | \\ CH(OH)CO.OH, \text{ a tribasic acid.} \\ | \\ CH_2CO.OH \end{matrix}$$
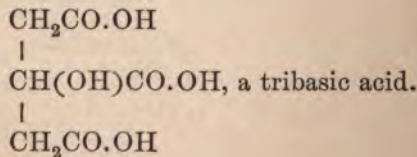
Esters. — It has been noted that the alcohols react with acids. In such reactions the hydrocarbon radical of the alcohol takes the place of the acid hydrogen with the formation of water. The product of the reaction is called an **ester** or **ethereal salt** from the analogy of the reaction to that by which salts of metals are formed from acids and bases. The esters, however, have none of the properties of salts. **Nitroglycerine** is an ester formed by the action of nitric acid on glycerine. It should properly be called glyceryl trinitrate, its formula being

$$CH_2(NO_3) - CH(NO_3) - CH_2(NO_3).$$
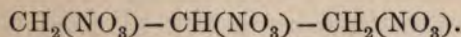
Esters are also formed from alcohols and organic acids, as when ethyl alcohol and acetic acid are heated together:

$$CH_3CH_2OH + CH_3CO.OH \rightleftharpoons CH_3CO.OC_2H_5 + H_2O.$$
$$\text{Ethyl alcohol} \qquad \text{Acetic acid} \qquad \text{Ethyl acetate}$$
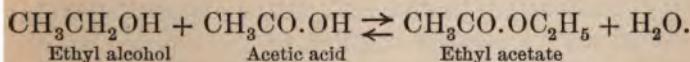
This reversible reaction may be brought to completion by the addition of a substance, like concentrated sulphuric acid, which absorbs the water as it is formed. Ethyl acetate has a pleasant, fruity odor, and its formation serves as a test for acetic acid or for alcohol. Many esters occur naturally in fruits, flowers, and other parts of plants, and are frequently the occasion of their characteristic taste and smell. Esters are also prepared artificially for flavoring perfumery, beverages, and foods; **methyl butyrate** is known as pineapple oil, **amyl acetate** as banana oil, etc.

Esters are hydrolyzed by water as indicated in the reversible reaction given above; and are decomposed by strong bases, such as sodium or potassium hydroxide,

with the production of alcohols and salts of the organic acids. Thus:

$$CH_3CO.OC_2H_5 + NaOH = CH_3CO.ONa + C_2H_5OH.$$
Ethyl Acetate   Sodium Acetate   Ethyl Alcohol
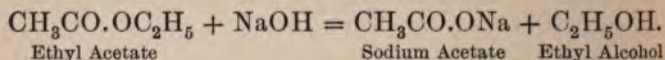
Fats and Soap. — Most of the natural fats and oils are esters in which the trivalent radical of glycerine, CH_2CHCH_2, has replaced the hydrogen in three acids: the **palmitic**, $C_{15}H_{31}CO.OH$, the **stearic**, $C_{17}H_{35}CO.OH$, and the **oleic**, $C_{17}H_{33}CO.OH$. The glycerine esters of the first two acids are solids, and that of oleic acid is an oil. The consistency of the fat depends on the proportions in which these three esters are present. Beef and mutton fat contain little glyceryl oleate, while olive oil consists mainly of this ester.

When fats are heated with water under pressure at about 200°, and then distilled in superheated steam, they are hydrolyzed into glycerine and the free acids. The oleic acid is separated from the solid acids by pressure, and the latter are used for making "stearin" candles.

Soap is made by boiling the fats with a solution of sodium or potassium hydroxide. The reaction is like that given above for ethyl acetate. In this case glycerine is formed, and a mixture of the organic salts of the alkali, which is soap. The potassium salts form "soft soap," the sodium salts "hard soap." The soaps are soluble in water, but by the addition of common salt to the solution of sodium soap it is precipitated ("salting out," see p. 259). Most of the salts of the organic acids of soap are insoluble in water, and hence, when soap is used with hard waters containing salts of calcium in

solution, insoluble organic salts of calcium are precipitated. This wastes soap, for no lather is formed and no cleansing effect is produced until the calcium is all precipitated.

The reaction by which soap is made is called **saponification**, and this term is used as a general one for the decomposition of esters by alkalies.

The Carbohydrates. — In this class of organic substances, hydrogen and oxygen, in the proportion in which these elements form water, are combined with carbon. They are not, however, hydrates, but contain the hydrogen and oxygen in hydroxyl and aldehyde groups. The sugars, starches, and cellulose are the most important members of this class.

Cane sugar is obtained from the sugar cane and from the sugar beet. It has the formula $C_{12}H_{22}O_{11}$. When boiled with water containing a little acid, the acid acts as a contact agent, producing hydrolysis of the sugar with the formation of two simpler isomeric sugars:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

<div style="text-align:center">Cane Sugar   Glucose or   Fructose
Grape Sugar</div>
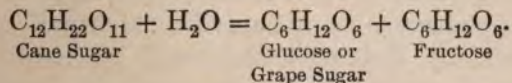
Both **glucose** and **fructose** occur naturally in fruits. **Lactose**, the sugar of milk, and **maltose**, produced by the action of malt on starch, have the same empirical formula as cane sugar. The sugars of the formula, $C_6H_{12}O_6$, are called **monoses**, and those of the formula, $C_{12}H_{22}O_{11}$, are called **bioses**.

Starch is found widely distributed in the vegetable kingdom. It is contained in large amounts in all grains, and in potatoes, etc. Its composition is repre-

o

sented by the formula $(C_6H_{10}O_5)_n$. The molecular formula is not known, but is undoubtedly a large multiple of the empirical formula. When boiled with dilute acids, starch is changed into dextrin and then into glucose, $C_6H_{12}O_6$, by hydrolysis.

Cellulose is the principal constituent of woody fiber. Linen, cotton, hemp, and flax are chiefly cellulose; paper which is made from cotton, linen, wood, and other plant fibers consists of cellulose, often with additions of various other substances. Ordinary filter paper is nearly pure cellulose, and the paper used in the laboratory for quantitative work contains scarcely a trace of other material. Cellulose has the same empirical formula as starch, and is usually represented, as this is, by $(C_6H_{10}O_5)_n$.

Fermentation. — A large number of chemical changes are brought about in organic substances under the influence of complex compounds secreted by living organisms, and are known as fermentations. The complex substances which occasion the fermentations are called **enzymes** and act as contact agents. They are produced by molds, by certain bacteria, and by yeast. Each enzyme brings about a change peculiar to itself. An enzyme of yeast causes the fermentation of grape sugar with the formation of alcohol and carbon dioxide as the chief products. Another enzyme contained in yeast changes cane sugar into a mixture of glucose and fructose, which then undergo alcoholic fermentation. Starch is converted into a sugar capable of alcoholic fermentation by the action of diastase, an enzyme formed in sprouting barley. These changes take place in the manufacture of alcohol and of beer. Alcohol in

dilute solution is oxidized by the acetic acid ferment into acetic acid ; and other enzymes convert milk sugar into lactic acid, and this into butyric acid.

Nitrogen Compounds. — Many organic compounds containing nitrogen, carbon, and hydrogen are known, which may be considered as substituted ammonias. In these, one or more atoms of the hydrogen in ammonia are replaced by hydrocarbon radicals, as in **methylamine**, CH_3NH_2, **aniline**, $C_6H_5NH_2$, **diethylamine**, $(C_2H_5)_2NH$, etc. These substances are basic, like ammonia, and form salts by direct union with acids, such as **aniline chloride** $(C_6H_5NH_3)Cl$, which is a substituted ammonium chloride.

The **alkaloids** are much more complex basic substances, many of which contain oxygen with the elements given above. Some of the best-known alkaloids are **quinine**, **strychnine, morphine**, and **cocaïne**.

The **proteins** form another group of complex nitrogenous substances which usually contain sulphur and sometimes phosphorus as well as carbon, hydrogen, oxygen, and nitrogen. Here belong albumen, gelatine, and other animal substances. The proteins are necessary to the food of animals. By putrefaction they produce poisonous substances called ptomaines, which resemble the alkaloids.

Another class of nitrogen compounds, made especially from benzene and its derivatives, are the **nitro-compounds**, in which the nitro-group NO_2 replaces hydrogen in an organic compound. The simplest of these is nitrobenzene, $C_6H_5NO_2$, which is made by the action of nitric acid on benzene, and which is converted into aniline by nascent hydrogen.

Among the many organic compounds which do not belong to the classes described is **urea**, $CO(NH_2)_2$. This may be regarded as carbonic acid, $CO(OH)_2$, in which each hydroxyl group is replaced by the amido-group NH_2. It is the chief compound in which nitrogen is eliminated from the body; and is of historic interest, because it was the first organic compound to be made from a substance not immediately derived from living organisms (Wöhler, 1828).

DESTRUCTIVE DISTILLATION

Destructive or dry distillation is the term given to the process of heating complex substances — usually organic substances such as coal or wood — by themselves in retorts, so that decomposition into simpler substances occurs without oxidation from the air.

Distillation of Coal. — Coal contains free carbon and also complex compounds of carbon with hydrogen, oxygen, and nitrogen, and almost invariably some sulphur compounds, — notably pyrites. When subjected to destructive distillation, these compounds break up and a large variety of volatile substances escape, leaving coke in the retorts. Some of the substances which come off are gases at ordinary temperatures, such as hydrogen, various hydrocarbons, ammonia, and hydrogen sulphide. If the gaseous product is to be used as **illuminating gas,** it is important to remove the ammonia and the hydrogen sulphide; for on burning the gas these would be oxidized into oxides of nitrogen and sulphur dioxide, which would be changed in the presence of air and moisture into nitric and sulphuric acids. The ammonia *is* all absorbed by dilute sulphuric acid, and most of

the sulphur by hydrated iron oxide, with which it re-
acts to form iron sulphide. The ammonium sulphate
produced in the gasworks as a by-product is the chief
source of ammonia and its compounds (p. 150), and the
sulphur from the hydrogen sulphide is recovered by a
process which regenerates the iron oxide, and is used
for making sulphuric acid. The purified gas consists
chiefly of hydrogen and hydrocarbons. Ordinary coal
gas contains about 50 per cent of hydrogen, 33 per cent
of methane, and 5 per cent of ethylene and other unsat-
urated hydrocarbons. One ton of good gas coal yields
about 10,000 cubic feet of illuminating gas, 1400 pounds
of coke, and 120 pounds of tar. The coal tar which is
produced is separated into a number of products by
further distillation, and these substances either find
immediate employment, or become the sources of a vast
number of important compounds, such as the aniline
and coal tar dyestuffs.

Distillation of Wood. — The volatile products from the
destructive distillation of wood are also both gases and
liquids. Among the latter are wood alcohol, acetic acid,
acetone, and creosote. The gases from wood are seldom
used for illuminating purposes, but are commonly burned
to supply heat for the retorts in which the wood is dis-
tilled. The residue in the retorts is charcoal.

Distillation of Bones. — Before distillation the fat is
usually extracted from bones by means of benzine or
carbon disulphide, and is used for soap making. The
chief products of the destructive distillation of bones
are ammonia, and bone oil which contains numerous
nitrogenous organic compounds. Bone black or animal
charcoal (p. 171) remains in the retorts.

Oil Gas is made from petroleum by causing it to drop on to red-hot iron plates in retorts, with the result that the hydrocarbons·of which it consists are broken down or " cracked " into simpler gaseous compounds. Oil gas is richer, or of higher illuminating power, than coal gas, and is employed to enrich coal gas and water gas. When burned alone, a special burner must be used to give a smokeless flame. Oil gas made by the *Pintsch process* is extensively used for lighting railway·cars, the supply being carried in steel cylinders in which the gas is stored under moderate pressure.

CHAPTER XVIII

SILICON AND BORON

SILICON

Silicon Dioxide or Silica. — Under the general name of quartz are included many minerals of differing appearance, such as rock crystal, flint, agate, amethyst, chalcedony, and jasper. Ordinary sand is usually pulverized quartz. All of these substances are essentially of the same composition and have the following properties: They are harder than glass, insoluble in water, and less fusible than platinum, melting only in the heat of the oxyhydrogen flame or that of the electric furnace. They are not attacked by any acid except hydrofluoric acid, and with this give a gas which reacts at once with water, forming a white precipitate of silicic acid and a solution of hydrofluosilicic acid. They react with fused potassium or sodium hydroxides or carbonates, producing a glasslike solid which is soluble in water ("water glass") and from whose solutions acids throw down a white gelatinous precipitate.

Fine white sand or any variety of pulverized quartz, when mixed with about an equal weight of magnesium powder and heated (in a test tube) until the mixture begins to glow, gives a mass from which, after repeated alternate treatment with hydrochloric, hydrofluoric, and sulphuric acids, a brownish powder is obtained, which is the elementary substance **silicon**. Silicon may be

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burned in oxygen, and yields an oxide which has the properties given above as characteristics of quartz. The composition of this oxide is represented by the formula SiO_2. A very large number of minerals and rocks may be proved to contain silicon by the reaction with hydrofluoric acid. Instead of using the prepared acid, the powdered substance may be mixed with powdered fluorspar and concentrated sulphuric acid, and gently heated in a platinum crucible. If a drop of water in a loop of platinum wire held in the mouth of the crucible becomes milky, silicon is present.

Silicon is, after oxygen, the most abundant element. It is always combined with oxygen, either alone, as in quartz, or together with metals in very many silicates. Silicon also occurs in certain plants, notably in the stalks of grains, in bamboo, etc., and in the feathers of birds. "Infusorial earth" or "tripoli" consists almost wholly of the siliceous shells of minute organisms. It is used as a polishing powder and as an absorbent for nitroglycerine in dynamite. Silicon dioxide in the form of sand is used on account of its hardness as an abrasive material, as in sandpaper, and in grinding glass and metals. It is also employed in making mortar, glass, and porcelain. At a very high temperature, quartz softens like glass, and may be formed, as this is, into flasks, crucibles, dishes, tubes, etc., which have the great advantage over glass utensils that they are more resistant to chemical action and withstand sudden extremes of temperature without breaking. A red-hot quartz vessel may be plunged into water without injury. This is due to the fact that quartz, after fusion, has a lower coefficient *of* expansion than any other known substance, about $\frac{1}{13}$

that of glass. Transparent quartz is made into lenses for spectacles and for other optical purposes.

Silicic Acids. — The gelatinous precipitate produced when an acid is added to a solution of water glass contains silicon with oxygen and hydrogen, probably in the form of hydroxyl compounds; but no well-defined single compound can be isolated. On separating and drying the precipitate, it loses water continuously, and is finally converted into the dioxide. The appearance of the precipitate is often delayed, and if the solution of water glass is poured into strong hydrochloric acid, the substance remains in solution. On placing this solution in a vessel whose bottom is made of parchment paper or animal membrane and is suspended in a large amount of water, the sodium or potassium chloride and the excess of hydrochloric acid pass through the membrane. The solution left in the vessel gives a jellylike solid on long standing or on evaporation, and this has the same indefinite composition as the precipitate thrown down by the acid. Substances of this gelatinous character, which behave in this way, are called **colloids**, and their solutions are called **colloidal solutions**. The process of separating colloids from other substances by means of a membrane is known as **dialysis**. A number of substances, which in their usual condition are insoluble, can be obtained in colloidal solutions. These solutions do not have the properties of ordinary solutions. Their freezing and boiling points are those of the pure solvent, and though the colloid passes through a filter, there is evidence to show that it is not dissolved in the usual sense, but is suspended in a state of fine division.

The colloidal solution of hydrated silica is supposed to contain the normal hydroxide of silicon $Si(OH)_4$, or **orthosilicic acid**. In changing to the gelatinous form, water is split off, giving, perhaps, $(HO)_2SiO$, **metasilicic acid**, and finally the dioxide SiO_2. The analyses of natural silicates show that many of them correspond to more complex silicic acids, which may be derived from two or more molecules of orthosilicic acid by the loss of the elements of water. Thus:

$$2\,H_4SiO_4 - H_2O = H_6Si_2O_7.$$
$$2\,H_4SiO_4 - 3\,H_2O = H_2Si_2O_5.$$
$$3\,H_4SiO_4 - H_2O = H_{10}Si_3O_{11}.$$
$$3\,H_4SiO_4 - 2\,H_2O = H_8Si_3O_{10}.$$
$$3\,H_4SiO_4 - 4\,H_2O = H_4Si_3O_8.$$
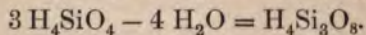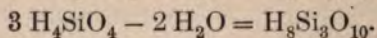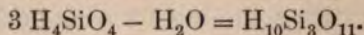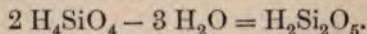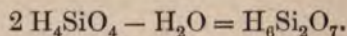
Olivine is Mg_2SiO_4, an orthosilicate; wollastonite is $CaSiO_3$, a metasilicate; serpentine, $Mg_3Si_2O_7$, a disilicate; and orthoclase, $KAlSi_3O_8$, a trisilicate. Opals are a mixture of various silicic acids. Among the well-known natural silicates are mica, kaolin and clay, feldspar, tourmaline, asbestos, and talc.

Silicic acid is a very weak acid, and is displaced from its soluble salts even by carbonic acid. The siliceous deposits from some geysers are due to the action of the carbon dioxide of the air on alkaline silicates which are dissolved in the geyser water. Some natural silicates are decomposed by hydrochloric acid, while others must be prepared for analysis by treatment with hydrofluoric acid or by fusion with alkaline carbonates. Artificial silicates of importance are glass, porcelain, and water glass.

Silicon Hydrides. — When the mass obtained by the reaction of silica and magnesium (p. 199) is treated with hydrochloric acid, bubbles of a spontaneously inflammable gas are given off. If a larger proportion of magnesium is heated with the silica, the gas is obtained much more abundantly. The magnesium takes the oxygen from the silica, and the silicon as it is set free combines with the excess of magnesium to form a silicide of magnesium:

$$SiO_2 + 2\,Mg = 2\,MgO + Si,$$

and $$Si + 2\,Mg = SiMg_2.$$
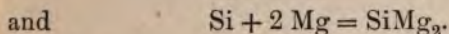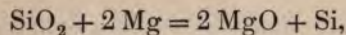
By the action of the acid on this silicide, the gas, silicon tetrahydride, SiH_4, is produced :

$$SiMg_2 + 4\,HCl = 2\,MgCl_2 + SiH_4.$$
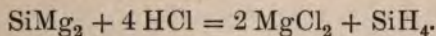
The spontaneous inflammability of the gas is due to small amounts of a liquid hydride, Si_2H_6, which is produced at the same time (*cf.* phosphine, p. 218). Silicon hydride is decomposed by heat into silicon and hydrogen, giving twice its volume of this gas :

$$SiH_4 = Si + 2\,H_2.$$
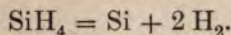
Silicon Halides. — Silicon fluoride, SiF_4, is produced when hydrofluoric acid (or a mixture of calcium fluoride and concentrated sulphuric acid) acts on silica or a silicate :

$$SiO_2 + 4\,HF = 2\,H_2O + SiF_4.$$
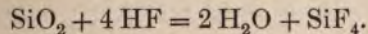
It is a gas which fumes in air and reacts at once with water with precipitation of silicic acid and the formation of soluble hydrofluosilicic acid :

$$3\,SiF_4 + 4\,H_2O = Si(OH)_4 + 2\,H_2SiF_6.$$
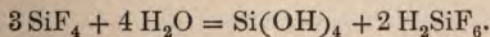
Hydrofluosilicic acid cannot be obtained except in solution, as on evaporation of the solution it breaks up into the two volatile substances, SiF_4 and HF.

Salts, however, of the definite composition which corresponds to the formula for the acid are readily prepared. The acid is used in analysis because of the slight solubility of its barium and potassium salts.

Silicon tetrachloride, $SiCl_4$, is made by the action of chlorine on a strongly heated mixture of silica and carbon:

$$SiO_2 + 2\,C + 2\,Cl_2 = SiCl_4 + 2\,CO.$$
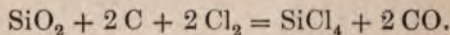
It is a colorless liquid boiling at 59°. It reacts at once with water, giving hydrogen chloride and silicic acid, and forms no complex acid as in the case of the fluoride. By passing the tetrachloride through an intensely heated porcelain tube containing silicon, the hexachloride, Si_2Cl_6, is produced. When silicon is heated in a current of hydrogen chloride, a compound of the formula $SiHCl_3$ is formed, which is analogous to chloroform. It is an inflammable liquid which boils at 34°.

Carbide of Silicon, SiC. — This substance, known as "carborundum," is made in the electric furnace by heating a mixture of quartz sand, coke, and common salt. It is not attacked by acids, even by hydrofluoric acid, but is decomposed by fusion with caustic alkalies. It stands next to the diamond in hardness, and is used as an abrasive material in grinding-wheels, whetstones, etc., and as a resistant substance for the lining of furnaces used in industrial operations.

Silicon. — Silicon may be obtained by the action of magnesium on silica, as already given, or by the reduc-

tion of the vapors of silicon tetrachloride by sodium or aluminium. It is now prepared in quantity by heating a mixture of quartz sand and coke in an electric furnace under special conditions. The molten silicon is cast in molds and used chiefly as a deoxidizing agent in refining steel and in making iron alloys. The commercial silicon contains from 90 to 97 per cent of silicon with iron and aluminium as the chief impurities. Silicon dissolves in many molten metals. With a number of these, such as magnesium and iron, it enters into combination, forming silicides, but separates out from others, such as silver and zinc, in crystalline form when the metals solidify. Silicon melts at 1400°–1500° and can be distilled in the electric furnace.

It burns with difficulty even in oxygen, combines with sulphur, and reacts with hydrogen sulphide and ammonia when heated. It reduces many oxides both of non-metals and metals at elevated temperatures.

Silicon is tetravalent in all of its compounds, and in this respect resembles carbon. Its analogy to carbon is most striking in the hydrides and halides, though here silicon shows only a slight tendency to form series of compounds like those of the hydrocarbons. Its oxide corresponds to carbon dioxide, and, like that, is an acid anhydride; but the many complex silicates find no analogies among the carbonates, and silicon forms no monoxide similar to that of carbon.

BORON

The substance which is well known under the name of borax is readily proved to contain sodium by the flame test. If a strong, hot solution of borax is treated

with sulphuric or hydrochloric acid and allowed to
cool, an abundance of white crystals is formed. These
are quite different from the crystals of borax, both in
appearance and in their soapiness to the touch. The
flame test shows that this substance does not contain
sodium, but it imparts to the flame a green coloration
of a characteristic tint, which indicates the presence of
some elementary substance we have not yet examined.
On heating the crystals, water is given off, and they
finally melt to a glassy solid which is unchanged by
further heating. Although the solution of the crystals
scarcely affects litmus, we may infer from the salt-like
character of borax that the substance has acid prop-
erties and that the product obtained by heating it is
an acid anhydride.

By the action of sodium or magnesium at a high
temperature, the substance is reduced and a brown amor-
phous powder obtained, which is the elementary sub-
stance **boron**, whose symbol is B, and whose atomic
weight has been found to be 11.

Preparation and Properties. — By heating the amor-
phous boron with aluminium, it may be obtained in
crystalline form. It is, however, difficult to prepare per-
fectly pure boron, and the crystals usually contain car-
bon and often aluminium. They are nearly as hard as
the diamond. Amorphous boron burns in oxygen with
the formation of the oxide, Bi_2O_3. This is its only ox-
ide, and the formula shows boron to be a trivalent ele-
ment. Burnt in air, boron gives some nitride with the
oxide. Boron also combines directly with chlorine and
with sulphur.

Boric Acid. — The substance which is obtained from

borax by the action of acids is **orthoboric acid**, whose formula is H_3BO_3 or $B(OH)_3$. At 100° it is slowly converted into **metaboric acid**, HBO_2, at 160° into the more complex **tetraboric acid**, $H_2B_4O_7$, and this, finally, at higher temperatures, into the **anhydride**, B_2O_3. These changes, which consist of successive losses of the elements of water, are shown by the following equations:

$$H_3BO_3 - H_2O = HBO_2;$$
$$4\,HBO_2 - H_2O = H_2B_4O_7;$$
$$H_2B_4O_7 - H_2O = 2\,B_2O_3.$$
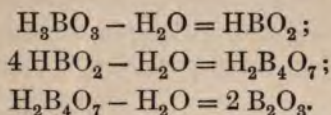
Borax $Na_2B_4O_7$, $10\,H_2O$, sodium tetraborate, is by far the most important salt of boric acid (*cf.* p. 268). Boric acid has antiseptic properties and has been largely used as a preservative for foods. When heated with metallic oxides it forms fusible metaborates, and on this account is used as a flux in brazing, etc. It is also employed in making enamels and glazes for pottery, but chiefly for the preparation of borax. It dissolves quite freely in hot water, but at ordinary temperatures the solution contains only about 4 parts of the acid in 100 of water. Consequently, when a hot saturated solution of it is cooled, the greater part of the acid crystallizes out.

The reaction by which boric acid is formed from borax is represented thus:

$$Na_2B_4O_7 + 2\,HCl + 5\,H_2O = 2\,NaCl + 4\,H_3BO_3.$$
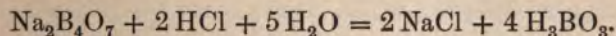
The chief natural compounds of boron are: borax, which is found in Borax Lake in California, and some other places; two or three minerals which are complex

borates of calcium and magnesium ; and boric acid, which occurs in the steam that issues from the ground in volcanic regions, notably in Tuscany, where the acid has long been obtained from this source.

Large amounts of boric acid are prepared from boracite, a double chloride and borate of magnesium which occurs in the Stassfurt salt deposits (p. 270), by treatment with hydrochloric or sulphuric acids.

Much of the boric acid is converted into borax by bringing it into a boiling solution of sodium carbonate :

$$4\,H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6\,H_2O + CO_2.$$
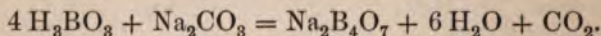
Other Compounds of Boron. — Boron fluoride, BF_3, is a gas which can be made by the action of hydrofluoric acid (or a mixture of calcium fluoride and concentrated sulphuric acid) on the oxide.   Like silicon tetrafluoride, which is made in a similar manner, it reacts with water, giving boric acid and hydrofluoboric acid :

$$4\,BF_3 + 3\,H_2O = H_3BO_3 + 3\,HBF_4.$$
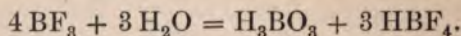
Boron has a great affinity for nitrogen, combining with it when heated in this gas to a white heat, forming the **nitride,** BN.   The nitride is more readily made by heating borax with ammonium chloride to redness:

$$Na_2B_4O_7 + 4\,NH_4Cl = 4\,BN + 2\,NaCl + 2\,HCl + 7\,H_2O.$$
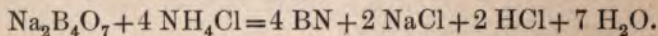
It is a white solid which decomposes when heated in steam into boric acid and ammonia.   A **carbide of boron,** B_6C, may be prepared by the union of boron and carbon at the temperature of the electric furnace.   It forms black crystals, and is one of the hardest of substances.

Detection of Boron. — Boric acid dissolved in alcohol colors the alcohol flame a characteristic green from the formation of a volatile ester. With small quantities, the color appears only on the surface of the flame. The same reaction is obtained from borates by adding sulphuric acid to set the boric acid free. Boric acid colors turmeric paper a reddish brown, which becomes more pronounced on drying the paper and is changed into a dark stain by alkalies. This is a characteristic and delicate test. The color is not affected by hydrochloric acid, so that this acid may be used to set boric acid free from borates. Boron shows no close analogies with other elements. In some respects its compounds resemble those of carbon and silicon, though its valence is different. On the other hand, it resembles aluminium, though it is a decided non-metal.

P

CHAPTER XIX

PHOSPHORUS AND ITS COMPOUNDS

PHOSPHORUS is an elementary substance which has
been used in several experiments. It is never found
free in nature, and is separated from its compounds with
so much difficulty that it is never made in the labora-
tory.

Common phosphorus is a slightly yellow, transparent
solid, of waxlike consistency at room temperature. It
melts at 44° and ignites at a little higher temperature.
When heated out of contact with air, it boils at 269°.
In moist air it evolves fumes of a garlic-like smell, and
is luminous in the dark. It owes its name to this last
property, which is due to its slow oxidation. The heat
developed in this oxidation is sufficient to cause a large
piece to finally melt and take fire. When finely divided,
it ignites instantaneously. This may be shown by
soaking a filter paper in a solution of phosphorus in
carbon disulphide ; the solvent quickly evaporates, and
the phosphorus left on the paper in minute particles at
once bursts into flame. Phosphorus is also easily kindled
by friction, and on account of the readiness with which
it ignites it is always kept under water and must be
handled with the greatest care. Phosphorus is practi-
cally insoluble in water, but dissolves freely in carbon
disulphide and some other liquids. Its atomic weight

is 31. The density of its vapor at temperatures up to a red heat indicates that its molecule contains four atoms.

Phosphorus is a powerful reducing agent, precipitating certain metals, such as gold and silver, out of solutions of their salts. It is very poisonous.

Red Phosphorus. — When phosphorus is burned in an inclosed volume of air, a reddish residue is left if there is more phosphorus than is necessary to unite with the oxygen. When this is burned in air, it yields the same product as that given by the ordinary phosphorus, and it is, therefore, another form of phosphorus. Common phosphorus may be wholly converted into the red modification by heating it to 240°–250° in an atmosphere free from oxygen, and the change takes place at lower temperatures if a trace of iodine is present. Red phosphorus is heavier than common phosphorus, is insoluble in the liquids which dissolve common phosphorus, is not poisonous, and does not change or ignite in air till heated to about 260°. On account of its inertness at ordinary temperatures, it is largely used in chemical operations in place of the common form. It does not have to be kept under water, and can be handled freely without danger.

Red phosphorus is the stable variety of phosphorus. It is changed into the yellow modification only by passing through the state of vapor. The change from yellow phosphorus to red is exceedingly slow at ordinary temperatures, as is shown by the time that yellow phosphorus can be kept ; and there is no definite transition temperature as in the case of monoclinic and rhombic sulphur.

Phosphorus Pentoxide. — The white solid, which is produced when either modification of phosphorus is burned, absorbs moisture with the greatest avidity, and is employed on this account as the most efficient agent for drying gases.   It is even able to withdraw the elements of water from many compounds, as is shown by its use in making nitrogen pentoxide from nitric acid (p. 136). Notwithstanding the difficulty of keeping it perfectly anhydrous, the exact weight produced from a known weight of red phosphorus has been successfully determined.   It is found that 1 gram of phosphorus yields 2.290 grams of the oxide.   One gram of phosphorus combines, therefore, with 1.290 grams of oxygen to form the oxide, and the formula derived from these figures by using the atomic weights, $P = 31$, and $O = 16$, is P_2O_5.

Phosphoric Acids. — Phosphorus pentoxide dissolves in water with a hissing noise and production of much heat.   The solution is acid, and when evaporated to a sirupy consistency gives, on cooling, a mass of deliquescent crystals of phosphoric acid.   This acid has the formula H_3PO_4, and is called **orthophosphoric acid** to distinguish it from related phosphoric acids which are formed from it by driving off the elements of water. When orthophosphoric acid is heated, it is converted into **pyrophosphoric acid**, $H_4P_2O_7$, and then into **metaphosphoric acid**, HPO_3 :

by t. $2\,H_3PO_4 - H_2O = H_4P_2O_7 ;$
    ignit $H_4P_2O_7 - H_2O = 2\,HPO_3.$
        dled
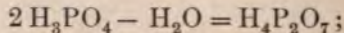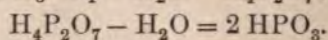
It is not p̶ insol ssible to change metaphosphoric acid into
    ̶ide le by heat.   Metaphosphoric acid is deli-
the pentoxi

quescent, and in solution gradually changes to the ortho-acid.

Phosphoric acid is made commercially by the action of dilute sulphuric acid on bone ash, which is chiefly normal calcium orthophosphate:

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4.$$
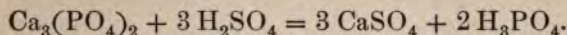
The phosphoric acid goes into solution and is filtered from the nearly insoluble calcium sulphate. The solution is then evaporated to dryness and heated to expel any excess of sulphuric acid. The acid is melted and is thus largely converted into metaphosphoric acid, which is cast in sticks. This acid is usually more or less impure. The pure acid is best made by the oxidation of red phosphorus with concentrated nitric acid. Glacial phosphoric acid is the meta-acid.

Orthophosphoric acid is a tribasic acid, and its salts are known as primary, secondary, and tertiary phosphates, according as one, two, or three of the hydrogen atoms are replaced. Ordinary sodium phosphate is a secondary phosphate, Na_2HPO_4, the other two sodium salts being unstable in solution. The tertiary phosphates of all metals except the alkalies are insoluble; but acid phosphates are soluble, and primary calcium phosphate, $CaH_4(PO_4)_2$, is largely used on this account as a fertilizer under the name of "superphosphate of lime." The tertiary phosphates are unchanged by heating, but the primary and secondary salts lose the elements of water and are converted into pyro- or metaphosphates:

$$NaH_2PO_4 = NaPO_3 + H_2O;$$
$$2\,Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$
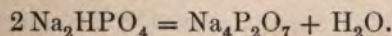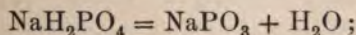
The reverse actions occur when the meta- and pyro-phosphates are dissolved in water.

Tests for the Phosphate Groups. — Silver nitrate solution, when added to solutions of orthophosphates or orthophosphoric acid, produces a yellow precipitate of Ag_3PO_4. With pyro- and meta-phosphoric acids and their soluble salts white precipitates are formed of $Ag_4P_2O_7$ or $AgPO_3$. Metaphosphoric acid can be distinguished from the pyro-acid by the fact that it coagulates a clear solution of albumen, while the pyrophosphoric has no effect on it. In solutions of orthophosphates the phosphate group PO_4 is also recognized by the precipitation of a white solid when a mixture of ammonium hydroxide, ammonium chloride, and magnesium sulphate is added; and in acid solutions of phosphates, by the formation of a dense yellow precipitate on adding a solution of ammonium molybdate in nitric acid. By these reactions the presence of phosphorus may be shown in many natural substances, since it always occurs in minerals as phosphate, and in organic substances is readily oxidized by concentrated nitric acid to phosphoric acid, while the organic matter is simultaneously destroyed.

Occurrence of Phosphorus. — Phosphorus is widely diffused in nature. In inorganic substances it occurs chiefly as phosphate of calcium. In this form it is found in apatite and other minerals; in guano, and in coprolite, both of which are of animal origin; and in the bones. Phosphorus is also a constituent of the tissues and blood of animals, and occurs in plants, where it is found especially in the fruits and seeds. Compounds of phosphorus, like those of nitrogen, are necessary to living

organisms.   They must be present in all fruitful soils, and are supplied to impoverished soils in fertilizers. The animals obtain their supply from their vegetable food or from the flesh of vegetable-eating animals. Phosphorus was discovered by an alchemist, Brand of Hamburg, in 1674, by heating evaporated urine with sand.   For one hundred years such phosphorus as was made was obtained in this way.   Brand kept his process secret, but it was discovered a few years later by Kunkel, in Germany, and by Boyle, in England.   The process was difficult and not always successful, and phosphorus was rare and costly.   In 1769 Gahn discovered the presence of phosphorus in bones, and a few years later Scheele published a method for making it from this material, which contains about 58 per cent of calcium phosphate.

Preparation of Phosphorus. — At present phosphorus is made both from bones and from mineral phosphates of calcium.   The inorganic matter of bones, which is left when bones are burned, consists almost wholly of normal calcium phosphate.   In order to utilize the bones as far as possible, they are usually not burned at once, but are either subjected to a process for the extraction of gelatine and then calcined, or are treated in closed retorts to obtain ammonia and bone oil, leaving bone black, or animal charcoal, which is used by sugar refiners for clarifying the sugar solutions.   When the efficiency of the bone black for this purpose is lost, it is burned to bone ash.   The former procedure for the manufacture of phosphorus from bone ash or from mineral phosphates was to produce an acid phosphate or phosphoric acid by the action of sulphuric acid, and then decompose

the phosphoric acid by means of charcoal at a high heat:

$$2\,HPO_3 + 6\,C = H_2 + 6\,CO + 2\,P.$$
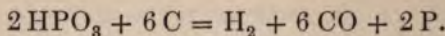
With the introduction of the electric furnace and the high temperature which it gives, it is possible to produce phosphorus directly from the normal calcium phosphate. In this process the phosphate is mixed with carbon and silica (sand) :

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C = 3\,CaSiO_3 + 5\,CO + 2\,P.$$
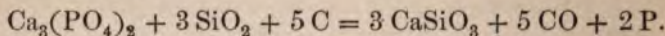
In both processes, the phosphorus vapors are delivered into cold water, in which solid phosphorus collects.   It is purified by melting it under water, and straining it, still under water, through canvas.   It is then redistilled.

Uses. — The greater part of the phosphorus which is produced is used in making matches.   Both common and red phosphorus are employed, the use of common phosphorus being forbidden in some countries because of its poisonous effects on the workmen.

Detection of Phosphorus. — Minute amounts of free phosphorus may be detected by distilling the material with water and using a glass condenser.   A luminosity in the dark appears where the steam condenses.

Phosphorous Oxide and Phosphorous Acid. — When phosphorus is incompletely burned in a limited supply of air, an oxide is formed which is more volatile than the pentoxide and can thus be separated from any pentoxide produced at the same time.   It is usually obtained as a waxlike solid which melts at $22.5°$.   Its composition is represented by the formula P_2O_3, but its vapor density shows that in the state of vapor the molecular

formula is P_4O_6. In air or oxygen it oxidizes at once to the pentoxide. Phosphorus trioxide dissolves in cold water very slowly with the formation of **phosphorous acid**, H_3PO_3; in hot water decomposition occurs with the separation of red phosphorus.

Phosphorous acid is also formed by the reaction of phosphorus trichloride on water (see p. 219). Its solution yields, on evaporation, a sirupy substance from which crystals of the acid separate which melt at 70.1°. It is a weak acid, and though it contains three atoms of hydrogen, only two of them can be replaced by metals to form phosphites, such as Na_2HPO_3. When strongly heated, the acid decomposes into phosphoric acid and phosphine:

$$4\,H_3PO_3 = 3\,H_3PO_4 + PH_3.$$
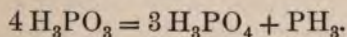
A still lower acid of phosphorus can be obtained which is known as **hypophosphorous acid**, H_3PO_2, which is a monobasic acid. This, like the phosphorous acid, gives phosphoric acid and phosphine on heating, phosphorous acid being formed as an intermediate step:

$$3\,H_3PO_2 = 2\,H_3PO_3 + PH_3.$$
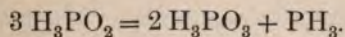
Both of these acids and their salts are reducing agents on account of their tendency to oxidize into phosphoric acid.

Phosphine, PH_3. — This is one of the products of the decomposition of hypophosphorous and phosphorous acids (see above), and is one of three compounds of phosphorus and hydrogen which can be made by indirect means. Phosphine is a colorless, ill-smelling, poisonous gas, while the other two hydrides are liquid

and solid. As usually prepared, phosphine contains vapors of the liquid hydride, which ignite at room temperature, so that the phosphine appears as a spontaneously inflammable gas.   It is made very simply by the reaction of calcium phosphide and water:

$$Ca_3P_2 + 6\ H_2O = 3\ Ca(OH)_2 + 2\ PH_3;$$
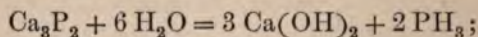
or by heating a solution of an alkaline hydroxide with common phosphorus in a flask from which the air should first be replaced by ether vapor or an indifferent gas, such as carbon dioxide, to prevent explosion:

$$3\ KOH + 4\ P + 3\ H_2O = 3\ KH_2PO_2 + PH_3.$$
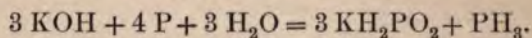
The gas is led into water, and as the bubbles break on the surface it burns with the production of a white cloud of phosphorus pentoxide which in still air forms fine vortex rings.   The only interest for us in phosphine, aside from this experiment, is in a certain analogy to ammonia which it shows in its formula and in the fact that it unites directly with hydrogen bromide and hydrogen iodide to form compounds which apparently contain the group **phosphonium**, PH_4, analogous to the ammonium group.   The phosphonium compounds are much less stable than ammonia and the ammonium compounds, decomposing with water into the hydrogen halides and phosphine.   The phosphine produced by the reaction of phosphonium iodide on potassium hydroxide is pure and not spontaneously inflammable:

$$PH_4I + KOH = KI + H_2O + PH_3.$$
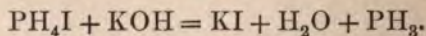
Phosphorus Chlorides. — We have seen that phosphorus takes fire at once in chlorine.   If the phosphorus

is in excess, the **trichloride**, PCl_3, is formed.   This is a liquid, boiling at 76°.   If the chlorine is in excess, or if chlorine is led into the trichloride, phosphorus **pentachloride**, PCl_5, is produced.   This is a white or yellowish solid, which, when heated, sublimes with partial dissociation into the trichloride and chlorine.

Both of these chlorides react with water and other compounds containing hydroxyl, producing compounds in which chlorine is substituted for hydroxyl; and also on many oxygen compounds with substitution of chlorine for oxygen:

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$
$$PCl_5 + H_2O = POCl_3 + 2\ HCl.$$
$$PCl_5 + SO_3 = POCl_3 + SO_2Cl_2.$$
$$PCl_5 + C_2H_5OH\ (alcohol) = POCl_3 + C_2H_5Cl + HCl.$$
$$PCl_5 + CH_3CO.H\ (aldehyde) = POCl_3 + CH_3CHCl_2.$$
$$PCl_5 + CH_3CO.OH\ (acid) = POCl_3 + CH_3CO.Cl + HCl.$$
$$2\ PCl_3 + 3\ CH_3CO.OH\ (acid) = P_2O_3 + 3\ CH_3CO.Cl$$
$$+ 3\ HCl.$$
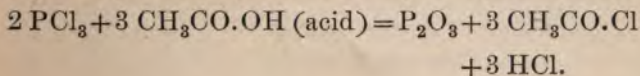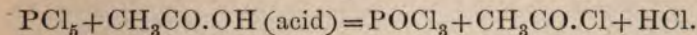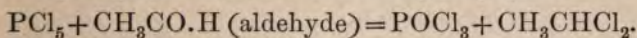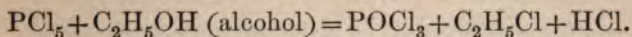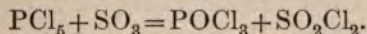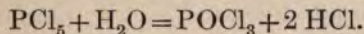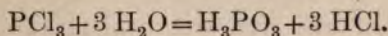
By means of such reactions it may be determined whether the oxygen in a compound is in the hydroxyl group or not; for an analysis of the resulting compound will show whether one atomic weight of chlorine has taken the place of one atomic weight of oxygen and one of hydrogen (hydroxyl), or two atomic weights of chlorine have replaced one atomic weight of oxygen.

Phosphorus oxychloride, $POCl_3$, which is formed in the reactions given above, is a liquid, boiling at 107°.

It decomposes with water, forming phosphoric and hydrochloric acids:

$$POCl_3 + 3 H_2O = H_3PO_4 + 3 HCl.$$
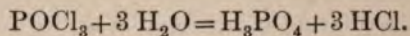
It also reacts with organic acids, replacing their hydroxyl with chlorine.

Phosphorus gives compounds with the other halogens which are like those with chlorine.

Phosphorus Sulphides. — Phosphorus unites with sulphur in several proportions. The sulphides are usually prepared by heating sulphur with red phosphorus, as the reaction with yellow phosphorus is violent. The so-called **sesquisulphide**, P_4S_3, is a pale yellow solid which is unaltered in air at ordinary temperatures, but takes fire at 100°. It is being used as a substitute for ordinary phosphorus in making matches which will light on any dry surface.

Matches. — The head of the common match contains certain oxidizing agents, such as manganese dioxide, red lead, and potassium chlorate, with a little phosphorus and antimony trisulphide as the combustible substances. These are held together with glue or dextrin. The sticks are prepared by dipping them into melted sulphur or paraffine. In the "safety" matches, the phosphorus is omitted from the match head and the striking surface consists of a layer of red phosphorus, antimony trisulphide, and glue. In the manufacture of the safety matches and of those in which phosphorus sesquisulphide is used in place of ordinary phosphorus, the danger of phosphorus poisoning is removed.

Valence of Phosphorus and Graphic Formulas of its Compounds. — The formulas of the oxides and chlorides of phosphorus show that this element is both trivalent and pentavalent. In the acids, as in all oxyacids, hydroxyl groups are believed to be present. The formulas of the pentoxide and of the acids related to it may be written graphically as follows:

$$O=P=O \qquad H-O-P \overset{/\!/O}{\underset{\backslash O}{}} \qquad \overset{H-O}{\underset{H-O}{>}}P=O$$

$$\overset{|}{O} \longrightarrow \overset{/\!/O}{\underset{\backslash O}{}} \longrightarrow \overset{|}{O} \longrightarrow 2\,\overset{H-O\backslash}{\underset{H-O/}{H-O-}}P=O.$$

$$O=P=O \qquad H-O-P \overset{/\!/O}{\underset{\backslash O}{}} \qquad \overset{H-O}{\underset{H-O}{>}}P=O$$

Pentoxide   Meta-acid   Pyro-acid   Ortho-acid
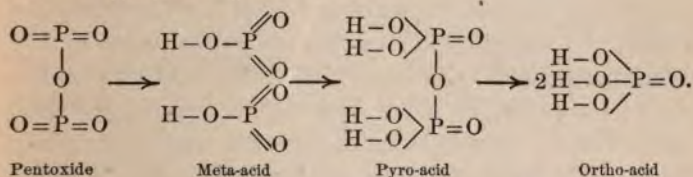
Phosphorous acid is written both $\overset{H-O\backslash}{\underset{H-O/}{H-O-}}P$ and

$\overset{H-O\backslash}{\underset{H/}{H-O-}}P=O.$ The second formula is preferred as a

record of the fact that phosphorous acid is only dibasic though it contains three hydrogen atoms, as the replaceable hydrogen of acids is considered to be always that of

hydroxyl groups. Phosphorous oxide is $\overset{P=O}{\underset{P=O}{>}}O.$ The graphic formulas of the chlorides and of phosphine are too simple to need illustration.

Acids as Hydroxyl Compounds. — We notice among the oxyacids we have studied that only in two instances are the number of replaceable hydrogen atoms and hydroxyl groups equal to the valences of the acid-forming element. These are the orthosilicic acid, $(HO)_4Si$, and the orthoboric acid, $(HO)_3B$. These acids both break

down with elimination of the elements of water into acids of less basicity; and other acids, such as ortho-phosphoric acid, undergo similar changes. In a general view of the acids we may consider all, except the ortho-silicic and boric acids, to be such derivatives of the highest possible hydroxyl compounds. Thus sulphuric acid may be derived from a "normal acid," $(HO)_6S$, by the loss of two molecules of water: $(HO)_6S - 2 H_2O = (HO)_2SO_2$; nitric acid, by the breaking down of the hypothetical $(HO)_5N$ into $(HO)NO_2$; and phosphoric acid from $(HO)_5P$. The first stable compound which results is the principal acid. In the case of sulphur, both $(HO)_6S$ and the first possible derivative $(HO)_4SO$ do not exist; in the case of nitrogen, $(HO)_5N$ and $(HO)_3NO$ are similarly unstable; while with phos-phorus we have a stable first derivative, $(HO)_3PO$. Or-thosilicic acid is very unstable, and boric acid is readily converted into the metaboric acid, $(HO)BO$. The more complex acids, such as many of the silicic acids corresponding to natural silicates, the tetraboric and pyrophosphoric acids are formed, as we have seen, by a similar process of elimination of the elements of water from two or more molecules of the simpler acids. Fi-nally some of the acids can be completely dehydrated by heating, and give oxides.

In the bases, which are hydroxyl compounds of the metals, the maximum number of hydroxyl groups is usually present; but here, too, where there are three or more hydroxyl groups, oxyhydroxides may be formed as: $Al(OH)_3 - H_2O = (HO)AlO$ or $HAlO_2$, and $Sn(OH)_4 - H_2O = (HO)_2SnO$.

These oxyhydroxides are usually unstable substances,

but their hydrogen can be replaced by metals with the production of more stable compounds which stand in the same relation to the oxyhydroxides that ordinary salts do to acids. The hydroxides of the metals suffer complete dehydration easily, all except those of the alkali metals being readily converted into oxides.

CHAPTER XX

ARSENIC, ANTIMONY, AND BISMUTH

ARSENIC

Arsenic Trioxide. — The substance which has long been known under the name of "white arsenic" is obtained as a by-product in the preliminary treatment of many ores which contain arsenides of the metals. This treatment consists in roasting (oxidizing) the ore to get rid of the arsenic, and the white arsenic appears as a smoke which is deposited in long flues or chambers leading to the chimney. It is purified by sublimation. It is sold in two forms : a white crystalline powder, and a porcelain-like substance. The crystalline variety sublimes readily, and if the vapors are condensed on a cool surface they return to the crystalline form; but if they condense on a hot surface, a vitreous mass is obtained, which at first is almost transparent, but after a time slowly becomes white and opaque on account of a gradual return to the crystalline condition. Both modifications are only slightly soluble in water, the vitreous modification dissolving more freely than the other. A saturated solution of the vitreous modification is unstable, crystals of the other variety separating out slowly. The solution is acid. Both modifications dissolve in hydrochloric acid more readily than in water, and when a hot, saturated solution of the vitreous modification is

cooled, the separation of crystals is accompanied with luminosity.

If a little white arsenic is mixed with charcoal and heated in a glass tube, a garlic-like odor is noticed, carbon dioxide is given off, and a black deposit is formed on the glass just beyond the heated part. This deposit, which appears as a metallic mirror, is the elementary substance, **arsenic**, and the experiment indicates that white arsenic is its oxide. This inference is easily confirmed by heating the arsenic in air or oxygen, when it burns, forming the characteristic octahedral crystals of white arsenic. If the reduction of the oxide is carried out quantitatively,[1] it is found that from 100 parts of the oxide 75.76 parts of arsenic are obtained; that is, that the oxide consists of 75.76 per cent of arsenic and 24.24 per cent of oxygen. Dividing these figures by the atomic weights of arsenic and oxygen, respectively, ($As = 75$, $O = 16$), we get the quotients, 1.010 and 1.515, which are in the ratio of $2 : 3$. The empirical formula is therefore As_2O_3, but the molecular weight derived from the vapor density shows that in the state of vapor, at least, the molecule should be represented by As_4O_6. It is, however, usually called **arsenic trioxide**, or **arsenious oxide**. Like all the soluble compounds of arsenic, the trioxide is a powerful poison. It is used in the manufacture of certain pigments and in glass making, and is the starting point for the preparation of other arsenic compounds.

Arsenious Acid. — This acid has not been prepared in the pure state, but is supposed to exist in the aqueous solution of arsenic trioxide, since stable salts called

[1] "Quantitative Experiments," page 67.

arsenites can be made, which correspond to a tribasic acid, H_3AsO_3. One of the best known is an arsenite of potassium which is used in medicine as Fowler's solution. "Scheele's green" and "Paris green" contain arsenites of copper. Both arsenic trioxide and the arsenites are reducing agents and are used as such in chemical operations. In effecting the reductions they are themselves oxidized to arsenic acid or arsenates.

Arsenic Acid. — H_3AsO_4, **orthoarsenic acid**, is usually prepared by warming the trioxide with nitric acid. It is a tribasic acid, closely analogous to phosphoric acid, and, like this, it may be changed by heating, and gives **pyroarsenic acid,** $H_4As_2O_7$, and **metarsenic acid,** $HAsO_3$. These changes occur at lower temperatures than with the phosphoric acids, and at nearly a red heat the metarsenic acid loses water, and is converted into the arsenic anhydride, or **arsenic pentoxide,** As_2O_5, while the metaphosphoric acid undergoes no such change. The pentoxide, metarsenic, and pyroarsenic acids when dissolved in water give at once the orthoarsenic acid.

The arsenates are very similar to the phosphates, and give precipitates of the same appearance with the magnesium mixture and with ammonium molybdate, but they form a reddish brown precipitate of silver arsenate on addition of silver nitrate. Arsenic acid is used in the manufacture of magenta, and its salts are employed in calico printing.

Arsenic. — Arsenic occurs in the free state in nature to some extent, but more commonly in combination with metals, as arsenides, or compound arsenides and sulphides, and in two sulphides, realgar, As_2S_2, and orpiment, As_2S_3. Recent investigations have proved that

arsenic compounds are very widely distributed.   They
are found in minute quantities in the primitive rocks,
in the sea and in mineral waters, in arable land, and in
plants and animals.   Arsenic is usually present in
pyrites and finds its way into the sulphuric acid made
by the chamber process from this source, and thence
into the many substances which are prepared by the use
of this impure acid.

Commercial arsenic is either the impure native arsenic
or more usually that prepared by heating arsenical py-
rites, FeSAs:

$$FeSAs = FeS + As,$$
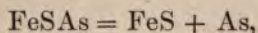
or by reduction of arsenious oxide by charcoal.

In its common form arsenic is a semimetallic sub-
stance; but it may be obtained in several modifications.
It sublimes without melting, giving a vapor whose den-
sity shows that, except at very high temperatures, its
molecule is As_4.   Arsenic is insoluble in water, but
oxidizes slowly in moist air, forming soluble com-
pounds which are poisonous.   Its use as fly poison de-
pends on this fact.   Heated in air or in oxygen it burns
to arsenious oxide.   It unites directly with the halogens,
giving halides analogous to those of phosphorus; it
combines readily with sulphur, phosphorus, and with
many metals, forming arsenides; but it forms no com-
pounds with nitrogen, boron, silicon, or carbon.
Arsenic is used in making shot, where it is added in
small quantity to the lead to render it harder.

Arsenic acts both as a triad and as a pentad element.

Hydrogen Arsenide or Arsine, AsH_3. — This is a gas
which is produced whenever nascent hydrogen acts on a
soluble arsenic compound.   To obtain it free from ad-

mixed hydrogen, zinc arsenide is treated with sulphuric acid:

$$Zn_3As_2 + 3\,H_2SO_4 = 3\,ZnSO_4 + 2\,AsH_3.$$
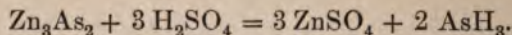
Its density is 2.695 (air $= 1$), which corresponds to the formula AsH_3. Arsine is unstable, being readily split into hydrogen and arsenic by heat, which agrees with the fact that it is an endothermic compound. It burns with a bluish white flame which gives off the trioxide as smoke. When a cold body is placed in the flame, brown or black spots of arsenic are formed, just as sulphur is deposited from hydrogen sulphide. The spots of arsenic dissolve in hypochlorites. Arsine is a reducing agent, precipitating silver from solutions of silver nitrate. It is an exceedingly poisonous gas.

Sulphides of Arsenic. — The natural occurrence of two sulphides of arsenic has been noted. The **disulphide**, As_2S_2, "realgar," is red, and the **trisulphide**, As_2S_3, "orpiment," is yellow. Both were formerly used as pigments. An artificial realgar is made at arsenic works by distilling a mixture of sulphur and arsenical pyrites and melting the sublimate obtained with sulphur, or by fusing white arsenic and sulphur in the proper proportions. The product, which is called "red arsenic glass," or "ruby sulphur," consists of the disulphide with an excess of sulphur. It is employed in pyrotechny as an ingredient of white fire, and in tanning, mixed with lime, is used to remove the hair from skins. An artificial trisulphide is also made by subliming a mixture of white arsenic and sulphur. The product is a mixture of the trisulphide and arsenious oxide and is very poisonous. It used to be employed as a yellow pigment, but has now given way to the much

less poisonous chrome yellow (p. 362). It is still used, however, in indigo printing and for some other purposes. Arsenic trisulphide is precipitated from solutions of arsenious acid and its salts by hydrogen sulphide, in the presence of hydrochloric acid, as a yellow precipitate. Arsenic pentasulphide is also formed as a yellow precipitate when hydrogen sulphide is led into solutions of arsenic acid or arsenates to which hydrochloric acid has been added. Both the tri- and penta-sulphides dissolve in solutions of alkaline sulphides with the formation of **thioarsenites** and **thioarsenates** in which sulphur appears in the place of oxygen in the arsenites and arsenates. In the precipitation of its sulphides arsenic resembles a number of the metals, and is therefore classed with the metals in the scheme of analysis. Arsenic may, in fact, be considered as a connecting link between the non-metals and the metals.

Detection of Arsenic. — On account of the readiness with which arsine can be formed, and its easy recognition by means of the properties which have been described, it is a valuable means of detecting arsenic. It is only necessary to put the suspected material, in which the arsenic is present as arsenious or arsenic acid, into a hydrogen generator. By leading the gas through a hard glass tube which is heated at one place, the arsine is decomposed and all the arsenic deposited on the cool glass beyond the heat. In this way the amount of arsenic in a weighed amount of the original substance may be determined.

Another and simpler method for detecting arsenic in papers, fabrics, or foods, consists in adding hydrochloric acid to the material and heating it with a strip of bright

copper. Arsenic is deposited as a dark film on the copper. After removing and drying the copper, it is heated in a glass tube, when the arsenic is oxidized and forms a ring of octahedral crystals of arsenious oxide on the cool part of the tube (Reinsche's test).

ANTIMONY

Antimony is a white solid of metallic luster and coarsely crystalline appearance. It is hard and so brittle that it may be readily powdered. It is somewhat lighter than zinc, and melts at a higher temperature than this metal. It does not tarnish in air, but when heated before the blowpipe burns with the production of white fumes. It combines directly with the halogens at room temperature, with sulphur when heated with it, and decomposes water at red heat. Nitric acid converts it into a white powder; aqua regia dissolves it; and hot concentrated sulphuric acid gives sulphur dioxide and a sulphate. Hydrochloric acid acts on pure antimony only in the presence of the oxygen of the air, but dissolves the commercial metal.

Antimony is used as a component of a number of alloys. Type metal is an alloy with lead and tin. The antimony imparts the necessary hardness, and the property of expanding as the melted alloy solidifies, so that sharp and accurate castings of the letters are obtained. Britannia metal and Babbitt's or anti-friction metal are other important alloys containing antimony.

Occurrence and Extraction. — Antimony occurs free to some extent, and is a constituent of a number of minerals in which it is combined with oxygen, sulphur,

or arsenic, or with sulphur and other metals, especially lead, silver, copper, nickel, and iron.

The sulphide, Sb_2S_3, known as stibnite, is the most abundant antimony mineral and the source from which the metal is prepared. The sulphide melts readily and is thus freed from the other substances with which it is mixed. It is then either fused with scrap iron which combines with the sulphur, setting the antimony free, or is roasted to convert it into the oxide, which is then reduced by carbon. The antimony thus prepared usually contains traces of other metals and some sulphide, and is purified by further treatment.

COMPOUNDS OF ANTIMONY

Antimony, like arsenic, has the valences of three and five. Very few antimony salts of oxygen acids are formed, and the principal compounds are those with oxygen, sulphur, and the halogens.

Halogen Compounds. — By the action of chlorine in excess on antimony, the **pentachloride,** $SbCl_5$, is formed. If the antimony is in excess, the **trichloride,** $SbCl_3$, is produced. The pentachloride is also obtained in solution when antimony is dissolved in aqua regia; and the trichloride results from the action of concentrated hydrochloric acid on the sulphide. This reaction is often employed for making pure hydrogen sulphide in the laboratory. The action is reversible, with the formation of the sulphide as an orange-red precipitate:

$$Sb_2S_3 + 6\,HCl \rightleftarrows 2\,SbCl_3 + 3\,H_2S.$$
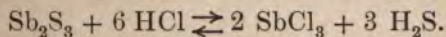
The pentachloride is a fuming liquid which is partly dissociated into $SbCl_3$ and Cl_2 on boiling at ordinary

pressure, but can be distilled unchanged in a partial vacuum. The trichloride is a soft, crystalline mass, formerly called "butter of antimony," which may be distilled without decomposition under ordinary pressure. The vapor densities of both of these chlorides have been determined and correspond to the molecular weights of their formulas. The trichloride is readily hydrolyzed with the formation of insoluble basic chlorides, such as SbOCl, and a clear solution is only possible in the presence of considerable hydrochloric acid. Hence if a solution of the trichloride is diluted with much water, a white precipitate appears.

Oxides of Antimony. — When the white insoluble powder formed by the action of strong nitric acid on antimony is carefully heated, a light yellow powder is obtained which is chiefly **antimony pentoxide**, Sb_2O_5. By the action of dilute nitric acid on antimony the principal product is the **trioxide**, Sb_2O_3, which is also formed by the direct oxidation of antimony. Both of these oxides when heated strongly in the air give the more stable **tetroxide**, Sb_2O_4. The tri- and pent-oxides are both acidic, but the acids which correspond to them are not as well characterized as those derived from the analogous oxides of arsenic. The insoluble product from the action of strong nitric acid on antimony is usually called **antimonic acid**, and given the formula H_3SbO_4.

Sulphides of Antimony. — The natural **trisulphide** of antimony, Sb_2S_3, is black and crystalline. The sulphide precipated from antimony solutions is an orange-red powder which, however, when heated changes to the appearance of the natural sulphide. The precipitated

trisulphide dissolves in a solution of yellow ammonium sulphide (polysulphide), forming a **sulphantimonate**:

$$Sb_2S_3 + 3\,(NH_4)_2S + 2\,S = 2\,(NH_4)_3SbS_4.$$
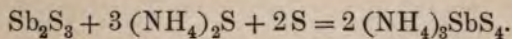
From this solution acids precipitate the orange **antimony pentasulphide**, Sb_2S_5, which is readily decomposed into the trisulphide and sulphur. Antimony pentasulphide is used in making red vulcanized rubber. The trisulphide is used as a component of match heads and as an orange pigment.

Antimony Sulphate, $Sb_2(SO_4)_3$, is obtained by the action of hot concentrated sulphuric acid on antimony or its oxides. It is readily hydrolyzed with the formation of insoluble basic sulphates.

Tartar Emetic is a soluble salt employed as a mordant and also in medicine, and often used for antimony reactions in the laboratory. It is a basic double tartrate of potassium and antimony, $K(SbO)C_4H_4O_6$. The monad group SbO is known as **antimonyl**, and the basic salts which contain it are called antimonyl salts.

Hydrogen Antimonide, or **Stibine**, SbH_3, is a gas similar to arsine, and formed under similar conditions. It has an odor slightly resembling hydrogen sulphide. It burns with a grayish flame which gives off white fumes of antimony oxide, and deposits black spots of antimony on cold porcelain. A mirror of antimony is formed when the gas is passed through a heated tube. The deposits of antimony are easily distinguished from those of arsenic. They differ in color and appearance, and the spots of antimony are not dissolved in dilute nitric acid or in a solution of bleaching powder, as the arsenic spots are. The antimony mirror does not vola-

tilize when heated as the arsenic mirror does, and when heated in a current of hydrogen sulphide, antimony yields the orange-colored sulphide, while the sulphide of arsenic is yellow.

Detection of Antimony. — The formation of stibine and the characteristics of this gas which have just been described may be employed for the detection of antimony.   Solid compounds of antimony give a brittle bead of the metal and a white incrustation, when heated with sodium carbonate on charcoal in the blowpipe flame.   The behavior of the metal towards acids, the precipitation of basic salts by water, and, particularly, the formation of the orange-colored sulphide are characteristic reactions.

Quantitative Experiment. — Conversion of antimony into the tetroxide (see *Quantitative Experiments*).

BISMUTH

Bismuth resembles antimony in appearance, but is distinguished from it by having a reddish tinge.   It is hard and brittle, but it is much heavier than antimony, and melts at a much lower temperature (264°).   It is unchanged in air, but when heated, burns to a yellow oxide.   It combines directly with the halogens and with sulphur.   Nitric acid, aqua regia, and hot concentrated sulphuric acid dissolve it.   Hydrochloric acid acts on it only in the presence of dissolved oxygen.

Bismuth is used as a component of a number of alloys of low melting points (fusible alloys) which serve as safety plugs for boilers and automatic sprinklers, and are used also for stereotyping and making copies of

wood cuts, etc., in which the property of expanding on solidification imparted to them by bismuth, and the low melting point, are both important advantages. Some of the alloys melt much below the boiling point of water and may be used for soldering under water.

Occurrence. — Bismuth is rather a rare metal. It occurs as oxide and sulphide and in a number of minerals, but chiefly in the metallic state. Native bismuth is occasionally quite pure, but is often alloyed with other metals. The ores are roasted, if they contain sulphur, and smelted with carbon and fluxes. The crude bismuth is then refined by taking advantage of its low melting point, or by fusion with various reagents which form compounds with the other metals.

Bismuth acts as a triad in its more important and stable compounds and is distinctly more metallic in character than antimony. It forms no compound with hydrogen. It is converted into the **trichloride** by chlorine or by aqua regia. No pentachloride is formed. The trichloride can be vaporized, and the vapor density corresponds to the formula $BiCl_3$. Nitric acid dissolves bismuth, forming the **nitrate**, which crystallizes as $Bi(NO_3)_3, 5\,H_2O$; and **bismuth sulphate**, $Bi_2(SO_4)_3$, is left as a white amorphous mass by evaporating a solution obtained by dissolving bismuth in hot concentrated sulphuric acid. All these salts are hydrolyzed by water with the formation of insoluble basic salts, and the crystallized nitrate, when heated, is changed into a basic nitrate. A basic nitrate precipitated by pouring a solution of the nitrate into a large amount of water is much used in medicine under the name of "subnitrate of bismuth."

Oxides. — Several oxides of bismuth have been obtained, but the **trioxide,** Bi_2O_3, is the most stable of them, and the others are all converted into this when heated in air.

Hydrated oxides are obtained by precipitating solutions of bismuth salts with alkalies, and they all give the trioxide when heated.

Bismuth trisulphide, Bi_2S_3, is precipitated from bismuth solutions by hydrogen sulphide. Unlike the sulphides of arsenic and antimony, it does not dissolve in solutions of the alkali sulphides.

Detection. — Bismuth or its solid compounds, mixed with sodium carbonate and heated before the blowpipe, give hard, brittle beads like antimony ; but the incrustation on the charcoal is yellow, and the beads dissolve in nitric acid. In solution, the dark brown color of the sulphide and its insolubility in yellow ammonium sulphide distinguish bismuth from antimony.

Quantitative Experiments. — Conversion of bismuth into the trioxide, and reduction of the trioxide to bismuth (see *Quantitative Experiments*).

COMPARISON OF THE ELEMENTS OF THE NITROGEN GROUP

The five elements, nitrogen, phosphorus, arsenic, antimony, and bismuth, both in their physical and chemical characters, and in those of their compounds, are a good illustration of the analogies and graded similarities which on a larger scale are found to run through the whole list of elements as tabulated in the periodic system.

Placing these elements in the order of their atomic weights from nitrogen to bismuth, we notice : that in physical state there is a progress from the gas nitrogen through the colorless or red phosphorus and the black, semimetallic arsenic to the antimony and bismuth, which, except in their brittleness, are thoroughly metallic in character ; that the specific gravities increase in the same order to that of bismuth, 9.8 ; that they all form compounds in which their valences are three and five, and which in general are analogous to each other. Members of both the triad and pentad series are well pronounced except in the case of bismuth.

All the group except bismuth form compounds with hydrogen of the type XH_3, but, while ammonia unites directly with all acids to form ammonium salts, phosphine forms such compounds only with the halogen acids, and arsine and stibine none at all. The halides of all of the group are hydrolyzed by water, though with those of antimony and bismuth the hydrolysis is incomplete. The oxides of the types X_2O_3 and X_2O_5 form acids with water except in the case of bismuth, the antimony trioxide being, however, more basic than acidic. Of these acids, those of phosphorus, arsenic, and antimony, derived from the pentoxides, exist in three varieties, — ortho, pyro, and meta, while the only nitrogen acid is that of the meta-variety, the theoretical ortho- and pyro-nitric acids being incapable of existence. The transition from the strongly pronounced nitric acid to the feeble acids of antimony is noteworthy. Bismuth trioxide is without acidic properties and acts as a base ; while the pentoxide behaves as a peroxide, reacting with acids to produce salts of trivalent bismuth

and oxygen, or giving chlorine with hydrochloric acid.
The elements of this group thus show in their chemical
behavior a gradual transition from pronounced non-
metallic characteristics to metallic characteristics, which
is in accord with their physical properties.

CHAPTER XXI

THE METALS — INTRODUCTION

SOME of the metallic elements have played important parts in a number of the reactions we have studied. Their hydroxides are bases, while the hydroxides of the non-metals are acids. In the reactions between acids and bases, or between acids and metals, the hydrogen of the acid is replaced by the metal with the formation of a salt. This replacing of acid hydrogen is the chief chemical characteristic of a metal. No sharp line of separation, however, can be drawn between the metallic and the non-metallic elements. We have seen in four related elements, phosphorus, arsenic, antimony, and bismuth, a gradual loss of non-metallic properties and the appearance of metallic characteristics. And we shall see, in other cases, that certain metals form hydroxides that are both basic and acidic, forming salts both with strong acids and with strong bases. The classification of the elements into non-metals and metals is, however, a convenient one for purposes of study.

Besides the general differences in chemical behavior, the metals as a class are distinguished from the non-metals by the following general properties.

General Properties. — Metals in compact form are opaque solids (except mercury), and their polished surfaces show a marked metallic luster. They are

usually malleable and ductile, and good conductors of heat and electricity, though differing widely in their possession of these properties. While tellurium, iodine, and graphite have a somewhat metallic-like luster, they, as well as the other solid non-metals in their usual modifications, are neither malleable nor ductile, but brittle and easily powdered, and poor conductors of heat and electricity. None of the metals, if we except arsenic and antimony, form volatile compounds with hydrogen; while all of the non-metals, except the argon group, give hydrogen compounds which are gases, or, as in the case of water, easily vaporized.

In the electrolysis of solutions of compounds of the metals, the metals usually appear at the negative electrode, while the non-metallic elements or groups are separated at the positive electrode. The metals, therefore, are electropositive as compared with the non-metals. We have seen that some metals are able to displace hydrogen in dilute acids, while these acids are without action on other metals. The rate at which hydrogen is evolved may be shown to depend on the nature of the metal, by making experiments with different metals in acid solutions of uniform strength. Further, it is found by experiment that if the metals which give the more rapid evolution of hydrogen are put in solutions of the less active metals, these are displaced and precipitated if they do not react with water; and finally, all the metals and hydrogen may be placed in such an order that each is displaced by those which follow it. The same order is found to hold good in the electrolysis of solutions of compounds of the metals, the **electromotive force** necessary to sepa-

rate any given metal from its solution being less than for any metal before it in the list, and greater than for any following it. This list is called the electromotive series and serves to classify conveniently other facts besides those mentioned. Thus the chemical activity in general follows the same order. Oxidation or rusting in the air takes place less and less readily as the metal stands lower in the series, until it ceases with copper The oxides of the metals down to magnesium are not reduced to metal by hydrogen; zinc and chromium oxides are reduced with difficulty; while from cadmium on, reduction takes place readily, and the oxides of the last four metals are changed into metals by heat alone. All the metals down to lead decompose water or steam with the production of oxides of the metals and hydrogen, the temperature for the reaction being higher as the metal is lower in the list.

Electromotive Series.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Antimony
Bismuth
Mercury
Silver
Platinum
Gold

Similar lists of the non-metals and acid groups may be made.

Other Properties. — Color. — All the polished metals in compact form are white or nearly white, except gold and copper. In a finely divided state, as the result of precipitation from solutions of their salts or reduction of their oxides, the metals are without luster, and gray or black in color; but when the powder is rubbed between hard surfaces the color and luster reappear.

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Crystalline Form. — Most metals can be obtained in crystals. Crystals are formed in many cases when the melted metal cools. Metals which are readily volatilized, such as zinc, crystallize from the state of vapor; while others separate in crystals when their solutions are reduced by other metals, as when zinc is placed in a solution of a lead salt. Some metals are also obtained in crystals when deposited from solutions of their compounds by electrolysis. In general, the crystalline form of the metals is one belonging to the so-called regular system, such as the octahedron or cube, or combinations of these.

Colloidal State. — A number of metals can be brought into a colloidal state (p. 201) by reduction from solutions of their compounds by phosphorus, ferrous sulphate, or some organic reducing agents; or by establishing an electric arc between two electrodes of the metal, under water. The colloidal solutions can usually be boiled without causing the metal to separate out; but the metal is precipitated when electrolytes are added; and is deposited at the anode when a current of electricity is passed through the liquid. In these collodial solutions the metals appear to be not dissolved, but in a state of extreme subdivision.

Other physical properties of the metals, specific gravity, hardness, malleability, tenacity, conductivity for heat and for electricity, the melting and boiling points, vary within wide limits. (See tables in the Appendix.)

Solubility. — While some of the non-metals are somewhat soluble in water, and some dissolve in carbon disulphide and other liquids, none of the metals are

soluble, as such, in any liquid except mercury. Many
dissolve in this, forming amalgams, and many, when
melted together, form more or less homogeneous mix-
tures which are called **alloys**.

Alloys resemble the elementary metals so closely in
appearance and general properties, that in common
usage no distinction is made between them and the
single metals. The properties of the alloys are in
some respects those which would be expected as the re-
sult of a physical mixture; but in other particulars they
differ widely from the mean or average of the properties
of the components. They are all solid except one of
potassium and sodium, but melt at temperatures which
are lower than the melting point of any of the com-
ponents. This is in accordance with what we have
learned about solutions, — that the freezing points are
lower than that of the pure solvent (p. 157), and allows
us to class some of the alloys as solid solutions.

The color of alloys is often not the average of those
of the components. Nickel coins contain 75 per cent
of copper and only 25 per cent of nickel, yet the color
has no suggestion of copper, while an alloy of aluminium
and copper containing 5 to 10 per cent of aluminium has
the color of gold. The modification of the properties of
metals which occurs in alloys makes it possible to pro-
duce "metals" having almost any desired properties.
Thus alloys may be made which shall melt at almost
any temperature and serve for fusible safety plugs in
steam boilers and for safety fuses in electrical work; or
a metal like copper, which is too soft and tenacious to
be worked in the lathe, by being alloyed with half its
weight of zinc is changed into brass which possesses

the necessary brittleness.   Gold and silver are too soft for coinage and are hardened by being alloyed with copper.   Lead is soft and yielding and contracts on passing from the molten to the solid state, while antimony is brittle and expands notably on solidification.   But by melting together one part of antimony and four parts of lead, type metal is produced, which is not brittle, is easily fusible, and expands at the moment of solidification, as is necessary for giving sharp castings of the letters. No other single metal or alloy has all of these properties.

The action of acids on alloys often differs from that on the component metals.   An alloy of platinum and silver is completely dissolved in nitric acid, in which platinum alone is insoluble ; while silver, which by itself dissolves readily in nitric acid, will not dissolve from an alloy consisting of silver with more than half its weight of gold.

Amalgams are formed by direct solution of metals in mercury; also by bringing mercury in contact with solutions of metallic salts (*e.g.* silver nitrate), or by making mercury the cathode in the electrolysis of a solution of a metallic compound.   The amalgams are in general like the alloys, but less stable.   Many amalgams find employment in the arts: tin amalgam for silvering mirrors, gold and silver amalgams for gilding and silvering, etc.

The Equivalents of Metals may be found by determining the amount of hydrogen which they displace from acids (or water),—their " hydrogen equivalents," [1] — or by making syntheses of their oxides, sulphides, chlorides, or other salts. [2]

[1] " Quantitative Experiments," p. 58.   [2] *Ibid.*, pages 62, 69, 72, 78, 84.

Atomic Weights of the Metals. — While none of the metals form volatile compounds with hydrogen, as the non-metals do, many volatile chlorides and organic compounds of the metals exist, whose vapor density determinations give a means for finding their molecular weights, and these may be used as an aid in deciding on the atomic weights of the metals.

A certain amount of assistance in fixing the atomic weights has been found in the probable similarity in molecular composition between salts which are isomorphous, — that is, which crystallize in the same form, and whose crystals grow in each other's solutions.

A means of some value in selecting the atomic weights of solid elements also lies in the fact, discovered in 1819, that a simple relation exists between their specific heats and their atomic weights.

Specific Heats and Atomic Weights. — It has been found that the specific heats (p. 31) of the solid elementary substances when multiplied by their atomic weights give approximately the same product. That is, the specific heats are inversely proportional to the atomic weights. Since the specific heats are values which are obtained by comparing equal weights of substances, and the numbers of atoms in equal weights of different elements must be inversely as the atomic weights, the statement may be put in this form: *The atoms of the solid elements all have the same heat capacity or specific heat.* This is known as the **law of Dulong and Petit.** A table giving the specific heats of a number of the metals is placed in the Appendix (p. 417). It is seen from this table that the variations from a constant value for the product of atomic weights and specific heats are con-

siderable, the mean value for the **atomic heat** being about 6.4.

When this relation between specific heats and atomic weights was once established by the examination of the specific heats of a number of metals whose atomic weights had already been fixed by other methods, it became possible to use it in selecting the atomic weight of other metals. This use of the law is like the use of Avogadro's hypothesis in finding molecular weights of gases and vapors by means of their densities, and is of particular advantage in the case of many metals which do not form readily volatile compounds. It should be noted that, as in the use of gas and vapor density determinations, the specific heat determinations do not serve to give the actual values, but only to indicate that the exactly determined equivalent, or some multiple of it, is to be taken as the atomic weight. In both cases approximate values for the specific heats, or vapor densities, are sufficient.[1] For instance, the equivalent of lead is found to be 103.55, and its atomic weight is either the same value or some multiple of it. A determination of the specific heat of lead gives 0.0310, and the average atomic heat, 6.4, divided by this specific heat, equals 206.4, which is so near to 207.1 (103.55 × 2) that it fixes this as the atomic weight of lead.

Molecular Weights of the Metals. — The greater number of metals boil at very high temperatures, and consequently the vapor densities of only a few of them have been determined. The molecular weights of zinc, cadmium, mercury, and silver which have been found in this way indicate that the molecules consist of single

[1] *Cf.* "Quantitative Experiments," pages 13 and 37.

atoms; the values for antimony and bismuth lie between those required for monatomic and diatomic molecules; and the density of arsenic shows that at very high temperatures the molecule consists of two atoms, but at lower temperatures, of four.

The molecular weights of a number of metals have been found from the lowering of the freezing point or the raising of the boiling point of such solvents as mercury or tin, and the results indicate that the molecules of most of these metals are monatomic.

Occurrence of the Metals. — The table of the occurrence of the elements (p. 418) shows that only six of the better-known metals occur in amounts of more than 0.1 % in the earth's crust.   These are, in the order of their abundance, aluminium, iron, calcium, magnesium, sodium, and potassium.   Many important metals do not appear in the table at all, being in the 0.5 per cent which includes " all other elements."   Some of our most valuable metals are here: gold, silver, platinum, tin, lead, and mercury; and in spite of their small relative amount, are in some cases the object of large industrial activities.

Only a few of the metals are found uncombined in nature, and these are always more or less alloyed with each other.   With the exception of two or three which occasionally occur free in rare minerals, these are the metals which follow hydrogen in the electromotive series, and are thus classed as metals of little chemical activity.   Most of the metals which are found in the free state occur also in compounds.   The usual natural compounds of the metals are oxides, sulphides, chlorides, carbonates, sulphates, and silicates.   The metals which

occur chiefly as salts are those at the top of the electro-
motive series down to and including aluminium, while
the most abundant compounds of those metals below
aluminium are oxides and sulphides. The rocks and
minerals which are used for the extraction of the metals
are called ores.

Extraction. — The mineral consisting of the metallic
compounds is first separated, if necessary, from the rock
which often accompanies it, and is then subjected to a
treatment which differs according to the nature of the
compound. **Oxides** are usually reduced by heating with
carbon, as is the case of the iron ores; **sulphides** and
carbonates are generally converted into oxides by roast-
ing, and the oxides reduced by carbon, or the sulphides,
after partial oxidation, are heated with the exclusion of
air, when the oxide and sulphide react to form sulphur
dioxide and the metal. In a few cases the metal is
separated by electrolysis of the fused compound. These
cover the principal methods used for the production of
metals. Other methods are employed in the laboratory
in special cases.

Early History. — The seven metals, gold, silver, cop-
per, tin, iron, lead, and mercury were known to the
ancients; antimony, bismuth, and zinc were known in
the 16th century or earlier; but the great majority of the
metals have been discovered within the last 125 years.

Those metals which occur free were naturally the
first to be recognized, and then those which were most
easily reduced from their ores. Thus, gold, silver, and
copper were probably the first metals known. Copper
was apparently the first metal employed for tools. After
the "copper age" comes a "bronze age" in which alloys

of copper and tin were used, and later, the "iron age."

The early metals were associated with the seven deified heavenly bodies in the astro-alchemical philosophy, and this is recorded in the names and symbols which were given them. Thus, gold, on account of its color and as the most perfect of the metals, was compared with the sun and given the symbol ☉. Silver was called "luna," a name which still survives in "lunar caustic," and received the symbol of the crescent moon, ☽. Copper, which was obtained from the island of Cyprus, the birthplace of Venus, was called by the name of this planet and represented by the symbol still used by the astronomers, ♀ ; its later name, "cuprum," from which we have the symbol Cu, comes from the place of its discovery. Iron was dedicated to Mars, with the symbol ♂ ; tin to Jupiter, ♃; lead to Saturn, ♄; and mercury to Mercury, ☿.

COMPOUNDS OF THE METALS

Oxides. — Most metals are oxidized when heated in air or in steam, but it is usually not easy to change the metal completely into oxide in this manner. The oxides of all of the metals except those of the alkalies (potassium and sodium), can however, be prepared indirectly by heating the hydroxides, carbonates, or nitrates. The quantitative synthesis of many of the oxides, giving data from which their formulas may be derived, is easily made by dissolving a known weight of metal in nitric acid, evaporating, and heating sufficiently to convert the nitrate into oxide.[1] Many

[1] "Quantitative Experiments," page 63.

metals form more than one oxide. Three classes of
these oxides are to be distinguished: **basic oxides**,
whose corresponding hydroxides are bases, and which
react with acids to form salts of the metals and water;
acidic oxides, which usually contain more oxygen than
the basic oxide of the same metal, and whose hy-
droxides act as acids (the same oxides are sometimes
basic towards strong acids and acidic towards strong
bases); and **peroxides**, which contain more oxygen than
the basic oxides, but are not acid-forming. The per-
oxides act as oxidizing agents, and give chlorine with
hydrochloric acid. Besides these well-defined classes
of oxides, many metals also form suboxides with less
oxygen than the basic oxides, and oxides which are in-
termediate in composition between the basic and acidic
oxides. The oxides are mostly insoluble in water; but
those of the alkali metals and alkaline earth metals re-
act with water to form hydroxides.

Hydroxides. — The hydroxides have a composition
which is equivalent to the oxides plus the elements of
one or more molecules of water. With the exception
of those of the alkali and alkaline earth metals, the
hydroxides are insoluble, and are, therefore, precipitated
when one of these soluble hydroxides is added to solu-
tions of the salts of the metals. Some of these pre-
cipitated hydroxides act as acids towards the bases
which precipitate them, and dissolve in an excess of
the alkali because of the formation of soluble salts.

Sulphides. — Many sulphides of the metals may be
made by the direct union of the metal and sulphur, or
by precipitation from solutions of their salts by hydro-
gen sulphide. The formulas of a few may be derived

from easily made syntheses.[1]   The sulphides generally correspond in composition to the oxides, and hydrosulphides are often formed in solutions, which are probably similar to the hydroxides.

Salts. — The salts of the metals are made by the action of acids on the metals or on their oxides, hydroxides, or carbonates.   Salts of non-volatile acids are also prepared by the reaction of the acid with a salt of a volatile acid, as in making sodium sulphate from common salt or saltpeter; and insoluble salts may be obtained by precipitation, as in the formation of barium sulphate from a barium chloride solution by sulphuric acid or a soluble sulphate.   Some of the halogen salts can be made by the direct union of the metal and the halogen.   The general characters of the salts have been briefly discussed under the various acids.

Carbides. — Carbides of the metals are formed by heating the metal or its oxide with carbon to a high temperature, usually in an electric furnace.   The different varieties of iron and steel owe their properties in part to the presence of carbide of iron.   Some of the carbides are decomposed by water with the production of hydrocarbon gases (*cf.* calcium carbide).

[1] " Quantitative Experiments," page 69.

CHAPTER XXII

METALS OF THE ALKALIES

FIVE metals, Sodium, Potassium, Lithium, Rubidium, and Cæsium, are grouped together because of the marked similarity which exists between their compounds. They are called the metals of the alkalies, or alkali metals, because their hydroxides all give alkaline solutions. They are all monovalent elements; and like other natural groups of elements, such as that of the halogens, show a gradation of properties in the order of the atomic weights. The following table shows the gradation of some of the physical properties of these metals, and their chemical activity follows the same order, gradually increasing as the atomic weights increase.

	ATOMIC WEIGHT	SPECIFIC GRAVITY	MELTING POINT	HARDNESS
Lithium . . .	7.00	0.534	186°	0.6
Sodium . . .	23.00	0.97	95.6°	0.4
Potassium . . .	39.10	0.86	62.5°	0.5
Rubidium . . .	85.45	1.53	38.5°	0.3
Cæsium . . .	132.71	1.87	26.5°	0.2

It will be noticed that the density and hardness of sodium and potassium would reverse the order which follows, their atomic weights. With this goes, perhaps,

the fact that the similarities between the compounds of
the last three elements are closer than between these and
the compounds of sodium and lithium.

General Characteristics. — At ordinary temperatures
these metals are soft, waxlike substances, whose freshly
cut surfaces tarnish immediately in the air.   They
stand at the head of the electromotive series and are
chemically the most active of the metals.   They all
decompose water vigorously, even at 0°, forming hy-
droxides which are the strongest bases.   The hydrox-
ides and carbonates of these metals are not decomposed
by heat, while all other hydroxides (except that of
barium) and carbonates of the metals break down into
oxides, with the separation of water or carbon dioxide.

The alkali metals and their compounds all give well-
marked and characteristic lines in the spectroscope, and,
as most of their compounds are soluble, this is the best
means of detecting and identifying these elements.

Sodium and potassium are by far the most abundant
of the alkali metals in nature, and many of their com-
pounds are of great importance in the industries and in
the laboratory.   Both of these elements occur in large
amounts in the feldspars and other natural silicates, and
by the slow but constant disintegration of these rocks
enter into the soil.   The sodium compounds are leached
out and find their way into the sea, while the potassium
compounds are largely retained in the soil.   Both potas-
sium and sodium compounds are taken up by plants,
the potassium compounds, at least, as an important factor
in vegetable growth.   Sea vegetation naturally contains
more sodium compounds than land plants, but the amount
of potassium compounds found in sea plants is all out of

proportion to their relative abundance in sea water. When vegetable substances are burned, the ash contains the carbonates of these metals. Both potassium and sodium occur as chlorides in large amounts, also as nitrates (saltpeters) and in smaller quantities in a number of other compounds. Their compounds are almost without exception soluble in water, and react readily with many other substances, being highly ionized. As a rule the potassium salts are less soluble than the sodium salts, and consequently the former are more easily obtained pure by crystallization. As potassium is more strongly positive than sodium, the potassium compounds are the stronger reagents, but the sodium compounds are not only cheaper weight for weight, but they "go farther" in chemical reactions because of the lower atomic weight of sodium. Thus, while the neutralization of 98 grams of sulphuric acid would require 112 grams of potassium hydroxide, only 80 grams of sodium hydroxide would be necessary. This fact often determines the choice of alkali compounds when the matter of cost comes in. But, on the other hand, certain differences in behavior may make the use of the potassium compounds imperative, as in making gunpowder, sodium nitrate being too hygroscopic for this employment.

SODIUM

Occurrence. — An examination of natural substances by the flame coloration and spectroscope shows that sodium compounds are universally distributed, and are present in all waters and in the dust of the air. The most important natural compound is common salt, whose composition has already been studied (p. 107). This salt

is not only used in large quantities for several well-known purposes, but also serves as the chief source for the production of many other sodium compounds and of the metal itself, as well as of hydrochloric acid and chlorine. It is present to the amount of 2.6 to 2.9 per cent in sea water, and in much larger quantities in certain confined seas, such as the Great Salt Lake in Utah, and the Dead Sea, — the latter containing nearly 8 per cent of this compound with other salts which make the total solids in solution about 26 per cent. Common salt also occurs in great deposits which are apparently the result of evaporation of prehistoric seas. The occurrence of sodium as nitrate (Chile saltpeter) and as borax have already been noted. Other natural compounds of importance are the fluoride, in cryolite, a mineral of Greenland, the sulphate, and carbonate. The manufactured compounds of sodium which find the most extensive uses are the carbonates, sulphate and the hydroxide.

Preparation and Uses. — Sodium was formerly made by heating a mixture of the carbonate or hydroxide and charcoal to a very high temperature; but it is now obtained by the electrolysis of the fused hydroxide, which, as it happens, was the way in which it was discovered by Davy in 1807. As sodium acts readily on water it is preserved in dry air in closed vessels, or more usually under kerosene. Its reaction with water has already been studied (p. 36). The metal finds industrial employment for making sodium amide, $NaNH_2$, a substance formed by reaction with ammonia; is used in the manufacture of indigo, and sodium cyanide, and as a source of sodium peroxide and pure sodium hydroxide.

The metal is also used as a reducing agent in the laboratory, especially in the form of sodium amalgam.

Oxide and Hydroxide. — When sodium is heated in a current of air to about 300°, the **peroxide**, Na_2O_2, is formed. The **monoxide**, Na_2O, can be prepared by heating sodium nitrate or nitrite with metallic sodium, nitrogen being set free. The monoxide is the basic oxide. It is very hygroscopic, and gives the hydroxide by direct union with water, and salts and water with acids. The peroxide is a yellow powder which does not deliquesce in air, but dissolves in water with evolution of oxygen and production of the hydroxide:

$$2\,Na_2O_2 + 2\,H_2O = 4\,NaOH + O_2.$$
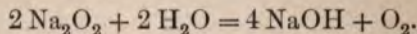
Hydrogen dioxide is formed as an intermediate product, and the reaction is only partial if the temperature is kept low. Sodium peroxide, like hydrogen dioxide, is a good oxidizing agent, and finds employment in various industries for oxidizing and bleaching, being sold under the name of "oxone." It is also a convenient source of pure oxygen in the laboratory. It absorbs carbon dioxide with the formation of sodium carbonate and oxygen gas, and its use has been proposed for regenerating the air contaminated by respiration in closed spaces, such as submarines.

Sodium Chloride. — Common salt is obtained from sea water and from salt deposits. In warm countries the sea water is concentrated by evaporation in the open air, either in shallow pools or by causing it to trickle down high hedges of brush; in cold countries, by allowing the water to freeze and removing the ice, which is almost wholly free from salt. In both cases

the salt is usually crystallized from the strong brine by means of artificial heat. The deposits of rock salt are sometimes mined like other mineral deposits, but more frequently water is conducted into the mines and the brine which is formed is pumped to the surface and boiled down. Occasionally the salt is crystallized by natural evaporation and is then known as "solar salt." The salt solutions are not evaporated to complete dryness, a "mother liquor" being left which contains the more soluble substances, and which is used as one of the sources of bromine. But the crystallized salt, nevertheless, is always more or less impure from the presence of sodium sulphate and calcium and magnesium chlorides. These last compounds are hygroscopic, and occasion the caking of table salt which has not been sufficiently purified. Pure sodium chloride can be made by neutralizing sodium hydroxide or carbonate with hydrochloric acid. It is also frequently prepared by leading hydrogen chloride gas into a saturated solution of salt. The pure salt is precipitated, while the impurities remain in solution, since salt is less soluble in a solution of hydrochloric acid than in pure water. An explanation of this precipitation is given in terms of the theory of ionic dissociation, which makes this only one of a number of cases under a general principle.

Ionic Equilibrium. — The molecular concentration of a solution is defined as the number of **gram-molecular weights** or **moles** (p. 51) of the substance which are dissolved in one liter. A solution containing 58.46 grams of sodium chloride in a liter would be of the same molecular concentration as one of sulphuric acid which contains 98.08 grams of the acid in a liter. In a

s

similar way we may speak of ionic concentrations, which
are equal when the weights of the ions in equal volumes
are in the ratio of their formula weights.   Now, accord-
ing to the ionic theory, every aqueous solution contains
a definite proportion of undissociated molecules and of
ions — or dissociated molecules.   The negative and
positive ions are always present in equivalent amounts.
In a solution of common salt, for instance, there will
be molecules of NaCl, with Na' and Cl' ions in equal
numbers.   If we call the concentration of the molecules
C and that of the ions C_1 and C_2, the ratio of the product
of the ionic concentration to the molecular concentration
will be a constant : $\dfrac{C_1 \times C_2}{C} = K$, and this ratio will

remain the same whatever the total amount of the dis-
solved substance.   If the solution is diluted, some of the
molecules will be dissociated into ions, and the molecu-
lar and ionic concentrations will both diminish ; but
C_1 and C_2 will diminish less rapidly than C, as the dilu-
tion proceeds.   If, on the other hand, the solution is
concentrated by evaporation, the concentration of the
molecules will increase more rapidly than the concen-
tration of the ions, some of these uniting to form
molecules.   The equilibrium will also be disturbed if
another compound, some of whose ions are the same as
those already present, is dissolved in the solution.
Suppose a solution containing NaCl, Na˙ and Cl' ions,
and that we add HCl, which at once gives H˙ and
Cl' ions.   Some of the Na˙ and Cl' ions must unite to
form molecules of NaCl in order to preserve the equilib-
rium.   Now if we start with a saturated solution, this
means that the newly formed molecules are in excess of

the solubility and must be precipitated. This, in brief
outline, is the explanation given by the theory of such
precipitations as that of salt, on addition of hydrogen
chloride. Another illustration of this principle is found
in the "salting out" of soap (p. 192). To be effective,
the added substance should be much more soluble than
the substance to be precipitated. The product of the
ionic concentrations, C_1 and C_2, in a saturated solution,
is called the **solubility product**. It has a constant value,
and when this is exceeded by the product of the con-
centrations of the ions, some ions unite to form a
precipitate. Thus the solubility product of the ions of
barium sulphate is very small; so whenever barium
ions and sulphate ions are brought together in excess of
this, as by adding barium chloride to a soluble sulphate,
barium sulphate is at once precipitated.

Sodium Hydroxide, NaOH. — Some discussion of this
compound has already been given. While it is obtained
pure by the action of sodium on water, the commercial
"caustic soda" is made either by boiling a solution of
sodium carbonate with milk of lime (calcium hydroxide
suspended in limewater), or by the electrolysis of a
solution of common salt. The reaction between sodium
carbonate and calcium hydroxide is a reversible reac-
tion:

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows 2\,NaOH + CaCO_3,$$
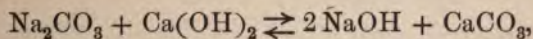
and, if the solution contains more than about 10 per
cent of sodium hydroxide, the reversal occurs. The
commercial product may be purified by dissolving the
solid hydroxide in alcohol, in which the impurities are
insoluble. The clear solution is evaporated to dryness

and finally fused in a vessel of silver. Vessels of common materials cannot be used in making pure hydroxide, because they are attacked by its solutions when strong and hot. Even the dilute laboratory solutions act on glass at room temperature, and it is a common experience to find the glass stopper of the sodium hydroxide bottle cemented in so that it cannot be removed. Sodium hydroxide is very soluble in water, and deliquesces in moist air, often becoming solid again from absorption of carbon dioxide and formation of carbonate. The solution has a caustic and decomposing action on animal substances. Next to potassium hydroxide it is the strongest of the bases. With the salts of other metals it generally forms hydroxides of the metals and the sodium salt of the acid. A similar action takes place with the organic salts or esters as in soap making (p. 192). Sodium hydroxide is largely used in soap making and in many other industries, and is an important reagent in the laboratory.

Sodium Chlorate and Hypochlorite. — When chlorine is led into a solution of sodium hydroxide, the products vary according to the temperature. If the solution is kept cool, the chief products are sodium hypochlorite and chloride ; but if hot, a further change occurs, producing sodium chlorate and chloride:

$$2\,NaOH + Cl_2 = H_2O + NaCl + NaClO\,;$$
$$3\,NaClO = 2\,NaCl + NaClO_3.$$
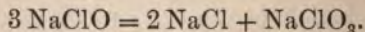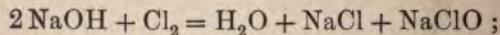
Both of these compounds are also prepared by the electrolysis of common salt solutions under proper conditions ; and the chlorate from calcium chlorate and

common salt. The immediate products of the electrolysis are, of course, sodium and chlorine, but the sodium at once reacts with the water of the solution to form sodium hydroxide. Hence sodium hydroxide is produced at the cathode and reacts with the chlorine set free at the anode according to the equations given above. The **hypochlorite** is an unstable salt, used in solution as a bleaching agent under the name of "Labarraque's solution." The **chlorate** is an oxidizing agent like potassium chlorate, but is far more soluble than this, and finds use for effecting some oxidations in solution.

Sodium Carbonates. — By far the most important of the manufactured compounds of sodium are the normal and acid carbonates. They are made in large quantities from common salt and in small amounts from cryolite. Two distinct methods are in use for the manufacture of sodium carbonate from salt: the older *Le Blanc process*, and its modern rival, the *Solvay* or *ammonia process*.

The Le Blanc Process. —This process, which was invented by Le Blanc at the time of the French Revolution, was the important process for more than one hundred years, but at present is very largely supplanted by the Solvay process. In the Le Blanc process the salt is first converted into sodium sulphate, the sulphate into sulphide, and finally the sulphide into carbonate. Salt is treated with sulphuric acid. The reaction occurs in two stages, the second requiring a high temperature :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$
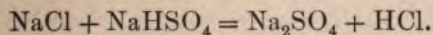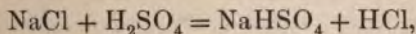
This is known as the *salt cake process*. An important modification, known as *Hargreaves's process*, avoids the use of sulphuric acid, and depends on the fact that sulphur dioxide in the presence of air and steam can transform salt into sulphate :

$$4\,NaCl + 2\,SO_2 + 2\,H_2O + O_2\;(air) = 2\,Na_2SO_4 + 4\,HCl.$$
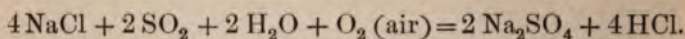
The Black Ash Process. — In this two reactions succeed each other in one operation. The salt cake, Na_2SO_4, is mixed with coal and limestone ($CaCO_3$) and heated. The sulphate is reduced by the coal to sulphide, which immediately reacts with the limestone to form sodium carbonate and calcium sulphide :

$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2,$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$
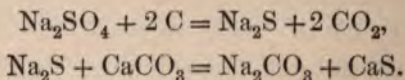
The end of the reaction is indicated by the production of carbon monoxide which is formed by the reduction of calcium carbonate by the carbon of the coal :

$$CaCO_3 + C = CaO + 2\,CO.$$
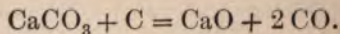
In this process it is found most effective to use more coal and limestone than the chemical equation requires, and consequently the black ash product contains not only sodium carbonate and calcium sulphide, but also considerable amounts of coal, limestone, and quicklime (formed from the excess of limestone by the high temperature), as well as smaller amounts of several other substances from impurities in the materials. The actual amount of sodium carbonate is considerably less than half of the weight.

Lixiviating the Black Ash. — As most of the other components of the black ash are insoluble in water, the sodium carbonate is separated from them by bringing it into solution. But here the lime brings about a re-action, changing a considerable part of the carbonate into hydroxide:

$$Na_2CO_3 + CaO + H_2O = 2\,NaOH + CaCO_3.$$
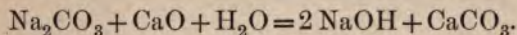
By leading carbon dioxide from lime kilns or furnaces into the solution, the hydroxide is changed back to the carbonate, and a number of impurities are precipitated. The clear solution is then evaporated to dryness and heated to convert it into crude anhydrous sodium carbonate, which is known as **soda ash**.

In the Le Blanc soda process we see that the materials used for accomplishing the conversion of common salt into sodium carbonate are sulphuric acid or sulphur, coal, and limestone; and that there are produced, as by-products, hydrogen chloride and calcium sulphide. The sulphuric acid is usually produced at the alkali works. The hydrogen chloride is dissolved in water, and most of the hydrochloric acid is used to make chlorine for the manufacture of bleaching powder. If the chlorine is made by the aid of manganese dioxide, this gives manganese chloride as by-product. Both this and the calcium sulphide are unmarketable.

The calcium sulphide contains all of the sulphur originally used for making the sulphuric acid or the sulphur dioxide of the Hargreaves's process. This sulphur can be recovered from the waste containing the calcium sulphide by the method of *Chance*, which depends on two reactions: 1. The action of carbon

dioxide and water on the calcium sulphide, with the
production of calcium carbonate and hydrogen sulphide.
2. The burning of hydrogen sulphide in a limited
amount of air to sulphur and water. The carbon diox-
ide is obtained from the lime kiln where limestone is
converted into quicklime for the purpose of making
caustic soda from the carbonate:

$$2\,CaS + H_2O + CO_2 = Ca(SH)_2 + CaCO_3\,;$$

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2\,H_2S\,;$$

then, $2\,H_2S + O_2 = 2\,H_2O + 2\,S.$
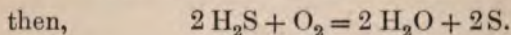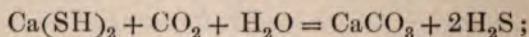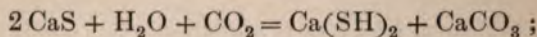
The manganese dioxide is regenerated by *Weldon's
process*. In this the manganese chloride solution, after
being freed from impurities by limestone dust, is treated
with milk of lime in excess, which precipitates manganous
hydroxide:

$$MnCl_2 + Ca\,(OH)_2 = Mn\,(OH)_2 + CaCl_2.$$
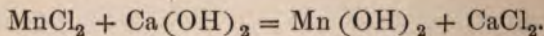
The hydroxide is then oxidized by pumping air
through the mixture, giving a "Weldon mud," which
will give chlorine with hydrochloric acid. This leaves
as final waste the comparatively valueless calcium
chloride.

The Solvay or Ammonia-Soda Process. — This process
depends for its success on the slight solubility of sodium
bicarbonate. The chemistry of the process is very
simple. Ammonia and carbon dioxide are led into a
concentrated solution of salt, and sodium bicarbonate is
precipitated while ammonium chloride remains in the
solution. We may consider the reaction as proceeding

in two phases ; first the formation of acid carbonate of ammonium :

$$NH_3 + H_2O + CO_2 = (NH_4)HCO_3;$$
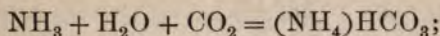
and then the double decomposition of the acid ammonium carbonate and the sodium chloride :

$$(NH_4)HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$
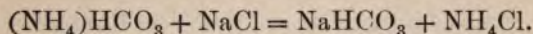
In practice the concentrated solution of salt is first saturated with ammonia, and then the clarified solution is treated with carbon dioxide.

The carbon dioxide for the first reaction is obtained by heating limestone, and the lime thus produced is used to recover the ammonia from the ammonium chloride which is formed in the second reaction :

$$CaCO_3 = CaO + CO_2;$$
and $$2 NH_4Cl + CaO = CaCl_2 + H_2O + 2 NH_3.$$
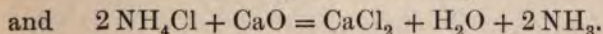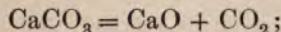
Thus the materials which are used are salt and limestone, and the products are acid sodium carbonate and the waste calcium chloride. The Solvay process is cheaper than the Le Blanc process and the product is purer.

The Cryolite Process. — A comparatively small amount of sodium carbonate is made from the natural double fluoride of aluminium and sodium known as cryolite. The cryolite is heated with chalk ($CaCO_3$) with the production of sodium aluminate, calcium fluoride, and carbon dioxide :

$$2 (NaF)_3 AlF_3 + 6 CaCO_3 = 2 Na_3AlO_3 + 6 CaF_3 + 6 CO_2.$$
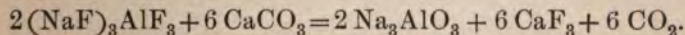
The sodium aluminate is dissolved in water and separated from the insoluble calcium fluoride, and the solution is treated with carbon dioxide, which precipitates

aluminium hydroxide, leaving sodium carbonate in solution.

Other Methods. — It is possible that the production of the carbonates of sodium from electrolytic caustic soda and carbon dioxide may become a commercial process. A little soda is made in some localities from the ash of seaweed, and it is also obtained from the waters of some soda lakes, such as Owen's Lake in California, by simple evaporation of the water.

Normal Sodium Carbonate usually crystallizes with ten molecules of water of hydration, $Na_2CO_3,10\ H_2O$, and in this form is commonly known as " washing soda." The crystals effloresce in the air, crumbling to a white powder which retains only one tenth of the water. Its solution is alkaline because of partial hydrolysis which produces sodium hydroxide, or, in the terms of the ionic theory, results in the formation of OH' ions. Enormous quantities of soda are used in the soap and glass industries.

Sodium Bicarbonate, $NaHCO_3$. — This is the first product of the ammonia process, and is readily made from the normal carbonate crystals by passing carbon dioxide over them. It is without water of hydration and readily loses carbon dioxide when heated, or when treated with even the weakest acids. For this reason it is used as a source of carbon dioxide for raising or lightening dough in cooking, under the name of " baking soda," or " saleratus," and as an ingredient of baking powders and effervescing preparations, such as Seidlitz powders and fruit salts.

Other Compounds of Sodium. — Of the other compounds of sodium a few of the more important may be *briefly* mentioned.

Sodium Nitrate, $NaNO_3$, which occurs as Chile salt-peter, is used in the crude form as a fertilizer for the sake of the nitrogen which it supplies to plants. It is also the chief source of nitric acid, and is used for making sodium sulphate, potassium nitrate, and sodium nitrite. The **nitrite**, $NaNO_2$, serves as a source of the nitrous acid which is used in making coal-tar dyes. It is made by the partial reduction of the nitrate when heated with lead (p. 135).

Sodium Sulphate, Na_2SO_4, which is produced as the first step in the Le Blanc soda process, and is a by-product in making nitric acid from Chile saltpeter, also occurs as a mineral, and in solution in natural waters. The anhydrous salt, known as "salt cake," is used in large quantities in glass making and in other industries. The salt crystallizes as Na_2SO_4, 10 H_2O, and in this form has long been known as " Glauber's salt " and used in medicine. It dissolves in water most freely at about 33°, and the solutions, on cooling, readily show the phenomenon of supersaturation (*cf.* p. 33).

Sodium Thiosulphate, $Na_2S_2O_3$, is prepared by boiling a solution of sodium sulphite or of caustic soda with sulphur:

$$6\,NaOH + 4\,S = Na_2S_2O_3 + 2\,Na_2S + 3\,H_2O.$$
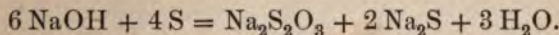
It crystallizes with 5 molecules of water, $Na_2S_2O_3$, 5 H_2O. When heated it decomposes into the stable sodium sulphate, sodium sulphide, and sulphur. Acids cause an evolution of sulphur dioxide and precipitation of sulphur. It is largely used as a fixing agent in photography under the name of "hyposulphite of soda," or "hypo," because it dissolves the silver salts which

would be darkened by exposure to light and spoil the picture. It is also used as an "antichlor," because of its reducing power, to check the action of chlorine in bleaching.

Sodium Cyanide, NaCN, is made in large amounts by passing ammonia over sodium heated to 300°–400°, and decomposing the sodium amide, $NaNH_2$, thus formed, by carbon at a red heat:

$$2\,Na + 2\,NH_3 = 2\,NaNH_2 + H_2;$$

$$NaNH_2 + C = NaCN + H_2.$$
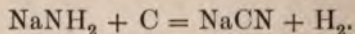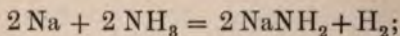
Sodium cyanide and also potassium cyanide are largely used for the extraction of gold, since weak solutions have the property of dissolving gold with the aid of the oxygen of the air.

Borax. Sodium Borate, $Na_2B_4O_7$. — An impure borax is imported from Thibet under the name of "tinkel." It is also obtained from Borax Lake and from deposits of calcium borate in California. The calcium borate is converted into the sodium salt by boiling with a solution of sodium carbonate, which precipitates calcium carbonate and leaves borax in solution. Much of the boric acid produced in Italy is also made into borax by means of sodium carbonate. Commercial borax is in two forms: prismatic borax, $Na_2B_4O_7$, $10\,H_2O$, and octohedral borax, $Na_2B_4O_7$, $5\,H_2O$, the former being the more common variety. This effloresces in the air, and when heated, loses its water, swelling into a spongy mass which melts at a red heat to "borax glass." Borax glass when heated with metallic oxides combines with them, forming fusible salts, and is thus useful as a flux for cleansing the surfaces of metals in brazing, solder-

ing, and welding. Octahedral borax does not swell up on heating and is on this account preferred as a flux. Some of the glassy metaborates of the metals have characteristic colors, and borax beads, formed in a loop of platinum wire, are employed in the laboratory to detect such metals as manganese, chromium, cobalt, etc. Borax is also used in making enamels and glazes for metal ware and pottery ; in soaps intended for use in hard water; as a food preservative ; and for many other minor purposes. Borax solutions have an alkaline reaction on account of hydrolysis.

Sodium and Potassium Silicates are both known as water glass. They are made by fusing the alkali carbonates or hydroxides with powdered quartz, SiO_2. Water glass is soluble in water, and is used for making artificial stone, cements, and soaps ; for fireproofing materials, and for many other purposes.

Sodium Phosphates. — Of the three possible sodium phosphates, the salt which commonly goes under that name is the disodium hydrogen phosphate, Na_2HPO_4, as it is the most stable. It is used as a laboratory reagent.

Quantitative Experiments. — Among the simple quantitative experiments which can be made with sodium and its compounds, and whose results may be used for determining equivalents or for deriving the formulas of the compounds, are : determination of the hydrogen equivalent ; conversion of sodium or its carbonate into chloride, nitrate, or sulphate ; of the chloride, or nitrate, or sulphite, into sulphate ; of the chloride into nitrate ; determination of the nitrogen in the nitrate. (See *Quantitative Experiments.*)

CHAPTER XXIII

POTASSIUM AND THE OTHER METALS OF THE ALKALIES

POTASSIUM

WOOD ashes contain about 10 per cent of potassium carbonate which can be separated from the other materials by leaching with water. This was formerly the chief source of the potassium compounds, and remains of some importance still in Russia, Sweden, and America. But now most of the compounds of potassium are derived from the immense deposits of potassium and other salts found at Stassfurt in Germany. This deposit is about 3000 feet thick, and some sixteen different salts have been found in it, — chiefly chlorides and sulphates of potassium, sodium, calcium, and magnesium. From these the chloride and sulphate of potassium are separated by methods of partial or fractional crystallization. Other, though minor, sources of potassium salts which are of interest, are : the molasses obtained in making beet sugar, and the scourings of sheep's wool. Metallic potassium and most of the salts of potassium are prepared by the same methods used for the sodium compounds, except that the ammonia process cannot be used for making the acid carbonate, as this is too soluble to be precipitated.

Potassium Nitrate, or saltpeter, KNO_3, was formerly obtained from natural or artificial saltpeter beds, where *it* is formed by bacterial action ; but this source is now

of little importance, as most of the salt is made from potassium chloride by double decomposition with sodium nitrate:

$$KCl + NaNO_3 = NaCl + KNO_3.$$
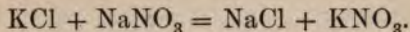
The success of this reaction depends on the fact that, of the four salts, sodium chloride is by far the least soluble in hot water and much of it is therefore precipitated. Potassium nitrate is very much less soluble in cold than in hot water, while the solubility of sodium chloride is about the same; consequently on cooling the solution, the greater part of the potassium nitrate crystallizes out. One or two recrystallizations are sufficient to free the nitrate from the little chloride which has formed with it. The composition and properties of saltpeter have already been studied (p. 130). Its chief use is in the manufacture of black gunpowder, where its place cannot be taken by the cheaper sodium nitrate because of the hygroscopic character of this salt.

Potassium Carbonate, K_2CO_3, known commercially as "potash" or "pearlash," is usually sold in the form of a white powder which is very deliquescent. It is the immediate source of the hydroxide and many other potassium compounds, and is used in making hard glass for laboratory purposes.

Potassium Hydroxide, KOH, is used in making soft soap, and as a stronger base than sodium hydroxide in laboratory reactions. Its commercial name is "caustic potash."

Potassium Bromide, KBr, and **Potassium Iodide**, KI, are made by heating strong solutions of potassium hydroxide with the halogens:

$$6 \, KOH + 3 \, Br_2 = 5 \, KBr + KBrO_3 + 3 \, H_2O.$$
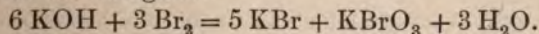
After evaporation, the mixture of bromide and bromate is heated alone or with powdered charcoal and the bromate is thus reduced to bromide.

Another method of making these halide salts is by first preparing the iron halides by direct union of the halogen with iron filings in the presence of water, and then obtaining the potassium salts by double decomposition with potassium carbonate. Both of the salts find important uses in medicine, and in photography, where they are used to form the light-sensitive halides of silver by reaction with silver nitrate. Potassium bromide and iodide are preferred to the sodium salts for most uses because they crystallize better and are more easily purified.

Potassium Chlorate, $KClO_3$, may be made by leading chlorine into a hot solution of potassium hydroxide:

$$6\,KOH + 3\,Cl_2 = KClO_3 + 5\,KCl + 3\,H_2O,$$
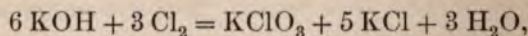
but as only one sixth of the hydroxide is utilized for chlorate, and the chlorate and the chloride are not easily separated, the practical method for the preparation of both potassium and sodium chlorates is by first making calcium chlorate by a similar reaction with the much cheaper milk of lime, and then converting this into the alkali chlorate by treatment with potassium or sodium chloride. The sodium chlorate is much more soluble than the potassium salt, and hence more troublesome to separate from the mixture. The chlorates are also made by the electrolysis of warm chloride solutions, conducted in such a manner that the chlorine set free at the anode comes in contact with the alkali formed at the cathode. Potassium chlorate is used as a source of oxygen in the

laboratory and as an ingredient of fireworks. Both salts are employed as oxidizing agents in the laboratory and in chemical industries.

Potassium Cyanide, KCN, is usually made by fusing the ferrocyanide (p. 339) with potassium carbonate :

$$K_4Fe(CN)_6 + K_2CO_3 = 5\,KCN + KOCN + CO_2 + Fe.$$
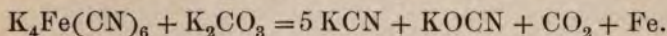
The cyanate, KOCN, may be reduced to cyanide by zinc. The anhydrous ferrocyanide, when heated in a closed crucible, also gives potassium cyanide :

$$K_4Fe(CN)_6 = 4\,KCN + FC_2 + N_2,$$
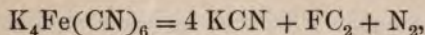
but the cyanide must be dissolved away from the iron carbide by alcohol or acetone, as with water a reaction between the compounds would occur with the re-formation of the ferrocyanide. Some other methods are employed, one of which depends on a reaction between carbon (charcoal), potassium carbonate, and ammonia at a red heat (*cf.* sodium cyanide, p. 267) :

$$K_2CO_3 + C + 2\,NH_3 = 2\,KCN + 3\,H_2O.$$
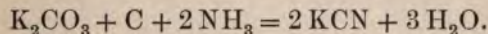
Potassium cyanide is a very poisonous substance and smells of hydrocyanic acid, as it is decomposed by carbon dioxide in moist air. It forms complex cyanides with the cyanides of other metals, which are often soluble. Such compounds are used for the solutions of gold and silver employed in electroplating. A dilute solution of potassium cyanide dissolves gold in the presence of air, and this is the basis of the cyanide process for extracting gold, in which large quantities of potassium cyanide are used. By melting potassium cyanide with sulphur, potassium sulpho- or thio-cyanate, KCNS, is formed, which is used as a delicate test for ferric iron.

T

Detection of Potassium. — Most of the potassium compounds are quite soluble, but a few, such as the acid tartrate, the fluosilicate, the perchlorate, and the chloroplatinate, are precipitated from solutions, which are not too dilute, by the corresponding acids. The perchlorate and the chloroplatinate are practically insoluble in alcohol, and these salts may be employed for the separation of potassium from sodium, and the determination of potassium. Potassium is readily detected even in very small amounts by the violet color which its compounds impart to the flame. This color is, however, masked by the yellow sodium flame color if small amounts of sodium compounds are present; but potassium may be detected in the presence of sodium by viewing the flame coloration through blue glass, or by means of the spectroscope.

Quantitative Experiments. — The conversion of the chloride, bromide, iodide, or carbonate into the nitrate or sulphate; the chlorate, perchlorate, or nitrate into sulphate; the carbonate, nitrate, chlorate, or perchlorate into chloride; and the determination of nitrogen in the nitrate. (See *Quantitative Experiments.*)

AMMONIUM

The ammonium compounds resemble those of potassium more nearly than those of sodium. The group NH_4, which plays the part of an alkali metal in the compounds, does not exist in the free condition. On electrolysis of a salt of ammonium with a mercury cathode, the mercury swells up to a pasty mass which gradually decomposes, even while forming, into mercury, hydrogen, and ammonia. The same substance is formed when sodium amalgam is put in a strong solution of an am-

monium salt, and it is fair to assume that the group NH_4 is present in the mass which is formed.   As only metals dissolve in mercury, the temporary existence of this ammonium amalgam supports the view of the metallic character of ammonium, which is suggested by the salts that it forms.   We have seen that ammonium compounds are found only in very small amounts in nature.   They are all readily made from ammonia or ammonium hydroxide by simple reactions. The behavior of ammonium compounds is in some respects different from that of the compounds of potassium or sodium, because of the instability of the ammonium group.   The halogen salts, the sulphate, and carbonate break up, when heated, into ammonia and acid, while the nitrate, nitrite, and some other salts suffer more deep-seated decompositions as we have seen (p. 147).   All the ammonium salts are decomposed by bases with the evolution of ammonia.

Ammonium Hydrogen Sulphide, $(NH_4)HS$, and **Ammonium Sulphide**, $(NH_4)_2S$, are made in solution by passing hydrogen sulphide into ammonia solutions. These solutions are much used in chemical analysis for the precipitation of sulphides of certain metals ; and have the advantage over the sulphides of potassium and sodium that any excess of the reagent may be expelled by boiling the mixture.   Ammonium sulphide dissolves sulphur, forming yellow polysulphides which are also used in analysis.

Ammonium Nitrate, NH_4NO_3, finds use as an oxidizing agent in fireworks and explosives, and is the source of nitrous oxide (p. 138).

Commercial Ammonium Carbonate is a mixture of the acid carbonate, $(NH_4)HCO_3$, and a substance known

as ammonium carbamate, $NH_4CO_2NH_2$, which may be regarded as normal ammonium carbonate from which a molecule of water has disappeared, or in which the amido-group NH_2 has replaced one NH_4O group:
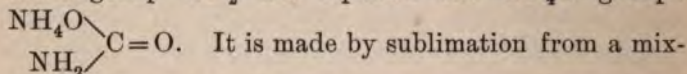
$$\begin{matrix} NH_4O \\ NH_2 \end{matrix} \Big\rangle C = O.$$ It is made by sublimation from a mixture of ammonium chloride or sulphate and powdered chalk. It is used as smelling salts or "salt of hartshorn." It is volatilized completely when heated, and was formerly called "sal-volatile."

When dissolved in water, the normal carbonate is formed, the reaction being reversible :

$$\begin{matrix} NH_4O \\ NH_2 \end{matrix} \Big\rangle C = O + H_2O \rightleftarrows \begin{matrix} NH_4O \\ NH_4O \end{matrix} \Big\rangle C = O.$$
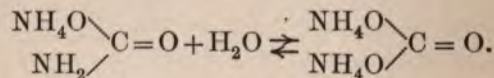
Crystals of the normal salt obtained from this solution smell of ammonia, absorb moisture from the air, and change into the more stable acid carbonate :

$$(NH_4)_2CO_3 + H_2O = (NH_4)HCO_3 + NH_4OH.$$
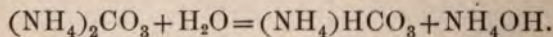
Ammonium sulphate, $(NH_4)_2SO_4$, made from the ammoniacal liquor of gas works, is largely used as a fertilizer, — Chile saltpeter and this salt being the principal inorganic substances by which nitrogen is supplied to cultivated soils. It is also a source of ammonia and its compounds.

Microcosmic salt, $Na(NH_4)HPO_4,4 H_2O$, sodium ammonium hydrogen phosphate, is converted by heat, first into sodium dihydrogen phosphate, and then into a glassy sodium metaphosphate, $NaPO_3$. This can unite with metallic oxides, giving characteristic colors with

some metals, and is used like borax in making bead tests.

Detection of Ammonium Compounds. — Ammonium compounds are readily detected by the ammonia which is evolved when they are heated with bases. The amount of ammonium may be determined by finding how much standard acid is neutralized by the ammonia evolved; or ammonium chloroplatinate, which like the potassium salt is insoluble, may be precipitated, and the amount of ammonium is easily calculated from the platinum left on its ignition.

THE OTHER ALKALI METALS

Lithium was discovered in 1817 as a constituent of certain minerals, and was given its name, which means stony, by Berzelius, who believed it to occur only in minerals, in contrast to potassium and sodium, which were found in plants and animal bodies as well as in minerals. It has since been found, however, that lithium compounds are widely distributed in minute quantities, and, finding their way into the soil by the disintegration of the rocks which contain them, are present in the ashes of many plants, such as the grapevine and tobacco, and in milk, human blood, and muscular tissues. Salts of lithium are also found in natural waters, and some mineral springs contain as much as 3 to 4 parts in 10,000.

Lithium is obtained in the form of chloride or carbonate by special treatment of the minerals in which it occurs, and the metal is quite readily prepared from the fused chloride by electrolysis.

The most notable **properties of lithium** are its low specific gravity, its ready combination with nitrogen,

and the brilliant red flame coloration which it gives. It is the lightest of all substances which are solid at ordinary temperature. It combines with nitrogen slowly at room temperature, and when heated in the gas gives the nitride, Li_3N, with incandescence. The flame coloration is so intense that the delicacy of the spectroscopic detection of lithium is second only to that of sodium.

Lithium carbonate and **phosphate** differ from these salts of potassium and sodium by being only slightly soluble. **Lithium chloride** may be separated from šodium chloride by the solubility of lithium chloride in a mixture of ether and alcohol, which hardly dissolves sodium chloride at all. Lithium spring waters and lithium carbonate are often prescribed for rheumatic affections.

Rubidium and **Cæsium** were the first elements discovered by the means of the spectroscope soon after its invention by Bunsen and Kirchhoff in 1860. Compounds of both occur in minute quantities, accompanying salts of the other alkalies, in minerals and in mineral springs. They were named from the colors of their spectroscopic lines, rubidium, red, and cæsium, blue. Their compounds are closely similar to those of potassium. Chemically both are more active and stand before potassium in the electromotive series.

CHAPTER XXIV

METALS OF THE ALKALINE EARTHS

" EARTH " is a term formerly used to designate substances which were unchanged by heat, were usually insoluble, and of an earthy appearance. Thus most of the oxides of the metals were earths. A few of those which are more or less soluble and whose solutions are alkaline were called alkaline earths, and this name is still retained for the oxides of barium, strontium, and calcium. These elements form a natural group, with a gradation in properties such as we have found in other groups of elements. Magnesia was one of the original alkaline earths, but the magnesium compounds are more nearly related to those of zinc.

	ATOMIC WEIGHT	SPECIFIC GRAVITY	HARDNESS	MELTING POINTS
Calcium . . .	40.09	1.52—1.59	1.5	800°
Strontium . . .	87.62	2 5	1.8	800
Barium	137.37	3.78	2.0	850

These metals stand next to the metals of the alkalies at the positive end of the electromotive series. They are all divalent elements. The chemical activity decreases from barium to calcium. They all decompose water at

room temperature with the formation of hydroxides which are less soluble than the alkali hydroxides, the solubility of calcium hydroxide being very slight.

The hydroxides and carbonates of calcium and strontium are converted into oxides by heating, while barium hydroxide and carbonate withstand all temperatures except that of the electric furnace.   The carbonates are changed into oxides at lower temperatures when mixed with powdered charcoal :

$$BaCO_3 + C = BaO + 2\,CO.$$
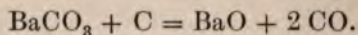
The oxides react energetically with water to form the hydroxides, and the hydroxides all absorb carbon dioxide with the production of carbonates.   The sulphates are reduced to sulphides when heated with carbon.   These sulphides are often luminous in the dark after exposure to light, and are used for luminous paint.   The luminosity appears to be due to the presence of traces of compounds of other metals.

The carbonates, sulphates, phosphates, oxalates, and fluorides of this group are insoluble or sparingly soluble in water.   While many of the compounds of calcium are of the greatest practical importance, and calcium itself is finding some applications, only a few of the compounds of barium and strontium are used, and these metals are prepared only as laboratory specimens.

CALCIUM

Reference to the table of the occurrence of the elements (p. 418) shows that calcium occurs in great abundance.   Its chief compounds are the carbonate, sulphate, fluoride, silicates and phosphate.   Besides

these minerals, the phosphate and carbonate are the
chief inorganic material of bones and shells.   Calcium
compounds are also found in all waters, chiefly as the
result of the solvent action of water containing carbon
dioxide absorbed from the air upon the natural carbon-
ates, and also as the slightly soluble sulphate.

The metal calcium, which used to be a laboratory cu-
riosity a few years ago, is now made commercially at a
moderate cost by the electrolysis of the fused chloride.
Calcium is about as hard as lead and cannot be cut easily
with a knife.   It tarnishes slowly in moist air, and de-
composes water, briskly at first, and then more and more
slowly unless the amount of water is very large, because
of the slight solubility of the hydroxide which is formed.
It acts vigorously on dilute acids.

Calcium carbonate, $CaCO_3$, occurs in a large variety
of mineral forms, as calc-spar, marble, limestone, chalk,
etc., and in dolomite, a double carbonate of calcium
and magnesium.   Calcium carbonate is insoluble in
water, but dissolves with evolution of carbon dioxide
in all dilute acids.   It is precipitated from neutral
or alkaline solutions of calcium salts by soluble car-
bonates :

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2\,NH_4Cl.$$
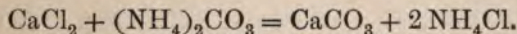
By the action of water containing carbon dioxide, it is
dissolved with the formation of a soluble acid car-
bonate :

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$
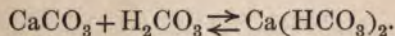
The reaction is so easily reversible that quite an excess
of carbon dioxide is necessary to effect the solution.

On boiling the solution, carbon dioxide is driven off and the normal carbonate precipitated. The "temporary hardness" of natural waters is due to the presence of this acid carbonate. Very hard water on standing often deposits some normal carbonate, and when hard water drops from the roofs of caves, icicle-like formations ("stalactites" and "stalagmites") are built up as the carbon dioxide escapes and water evaporates. Calcium and magnesium sulphates, which are often present in natural waters, confer a permanent hardness, in the sense that it is not removable by boiling. Soap (p. 192) reacts with hard water, forming insoluble calcium salts of the organic acids of the soap, and does not produce a lather until all the calcium has been removed from solution. The degree of hardness of a water is determined by the amount of soap necessary to form a persistent lather. Hard waters are not only wastful in soap, but also cause much trouble in steam boilers because of the amount of solid which accumulates as a boiler crust. By adding a calculated amount of milk of lime to a hard water, the calcium present as temporary hardness may be all precipitated :

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\,CaCO_3 + 2\,H_2O.$$
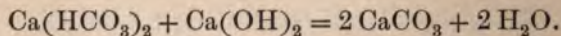
When heated sufficiently, calcium carbonate dissociates into carbon dioxide and calcium oxide. The reaction is reversible :

$$CaCO_3 \rightleftarrows CaO + CO_2,$$
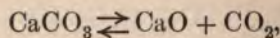
and as in all such reversible reactions, the progress in *one* direction or another depends on the temperature

and concentration (*cf.* p. 69). Limestone and chalk are used in a number of chemical operations on the large scale and are the chief source of the other compounds of calcium. On account of the dissociation which occurs, calcium carbonate at high temperatures may act like calcium oxide.

Calcium Oxide and Hydroxide. — The oxide, which is commonly known as *lime* or *quicklime*, is made by heating some variety of calcium carbonate to a bright red heat (800° to 900°). The operation is carried out commercially in kilns in which the necessary heat is produced by burning coal or fuel gas. It is essential that the gases shall issue freely from the kiln on account of the reversible character of the reaction. The carbon dioxide which is formed is sometimes utilized, as in the Solvay soda process, but it is more often allowed to escape.

Pure calcium oxide is infusible at the temperature of the oxyhydrogen flame, and cylinders of it are used for producing the "limelight." It unites energetically with water and forms the hydroxide or "slaked lime":

$$CaO + H_2O = Ca(OH)_2.$$
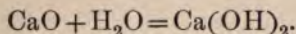
Quicklime is used on this account as a dehydrating agent, as in making "absolute" alcohol and in drying certain gases. The heat which is developed in this reaction is so great that combustible substances may be kindled. Hence there is a certain amount of danger in the storage and transportation of lime. In the air, moisture and carbon dioxide are absorbed with the formation of carbonate, and lime which has in this way become "air-slaked" is unfit for making mortar.

A.KEAN

The composition of calcium oxide may be established by converting a known weight of the metal into oxide. This cannot, however, be done successfully by burning the metal in air, as it is difficult to burn it completely; but by first making the nitrate and then decomposing this by heat, the oxide is readily formed.[1] It is found to consist of 28.53 per cent of hydrogen and 71.47 per cent of calcium. From these figures the equivalent of calcium (oxygen = 8) is found:

$$28.53 : 71.47 : : 8 : \text{equivalent} = 20;$$

and the formula derived in the usual way is CaO. Since the carbonates can be decomposed into calcium oxide and carbon dioxide, a determination of the weight of carbon dioxide which can be obtained from a known weight of the carbonate, with the knowledge of the composition of CaO, serves to establish the formula of the calcium carbonate as $CaCO_3$.

When lime is slaked in much water, a milky fluid results which is called "milk of lime." It consists of a weak though saturated solution of the hydroxide, and suspended particles of solid hydroxide. On standing, the solid settles out, leaving a clear solution of "lime-water" which is used in the laboratory as a test for carbon dioxide:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
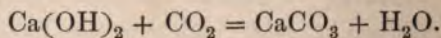
Calcium hydroxide, both in the solid state, and as milk of lime, is largely used as the cheapest base in chemical industries, as in making chloride of lime.

Mortar. — A large industrial use of lime is for making mortar. The quality of the lime varies with the

[1] "Quantitative Experiments," pages 63 and 64.

nature of the limestone from which it is made. If this is nearly pure calcium carbonate, the lime slakes readily and is called " fat " lime, while lime which contains much impurity slakes slowly and gives a poor mortar. Slaked lime alone does not serve as mortar, because it shrinks too much on drying and becomes too compact. Mortar is always made from a mixture of slaked lime and sharp sand, the sand preventing undue shrinkage and keeping the mortar porous, so that the carbon dioxide of the air can penetrate. The " setting " of mortar is due to the evaporation of water and its absorption by the bricks; the mortar then slowly absorbs carbon dioxide from the air, which gradually converts the hydroxide into carbonate. In this hardening of the mortar water is continually formed, and consequently freshly plastered rooms are damp.

Cements are composed of anhydrous double silicates of calcium and aluminium which can combine chemically with water to form a hard mass, and do not, like lime, require the presence of carbon dioxide for hardening. They are chiefly made from clay limestones, or from mixtures of pure limestone and clay, which are " burned " in the same manner as in making lime. The product is ground to a fine powder; and when mixed to a paste with water immediately begins to set and harden, even under water.

Hydraulic Mortars are mortars which are made from limestone containing more than 8 per cent of clay. They contain free lime, but will set and harden under water like the cements.

Calcium Sulphate occurs naturally as gypsum, $CaSO_4, 2 H_2O$, and less abundantly as anhydrite, $CaSO_4$.

The sulphate is so slightly soluble in water that it is precipitated from all solutions of calcium salts, except the most dilute, on addition of a more soluble sulphate or of sulphuric acid. Calcium sulphate is readily made from the metal and its other compounds by sulphuric acid, and as it withstands a mild red heat at which the other compounds formed in the reaction and the excess of sulphuric acid are driven off, it may be used in a quantitative determination of calcium, or for fixing the equivalent of the sulphuric acid group to calcium, and to other elements or groups which are displaced by the acid.[1]

When gypsum is heated to 125° it loses most of its water of hydration and becomes " plaster of Paris." This substance, as is well known, when mixed to a paste with water soon hardens; and, as it expands in hardening, it fills all lines and angles of a mold, giving faithful reproductions.   Besides its large use in making plaster casts, it finds employment for ornamental plaster work and as a cement.   " Stucco " is made of plaster of Paris with rubble and glue or size.   If gypsum is heated to a higher temperature than that given above, so that all of its water is driven off, it no longer sets and hardens. It has been found that properly made plaster of Paris consists chiefly of a slightly hydrated salt, $2\,CaSO_4,H_2O$, which contains one quarter as much water as the gypsum, and which is more soluble than the gypsum or the anhydrous sulphate.   When mixed with water this salt dissolves, making a solution which is supersaturated with respect to the hydrate.   As some crystals of the hydrated salt are present, however, the state of supersaturation

[1] " Quantitative Experiments," pages 85–87.

cannot exist and crystals of $CaSO_4,2H_2O$, separate. The water dissolves more of the $2CaSO_4,H_2O$, which crystallizes as gypsum, and finally the whole is converted into gypsum in the form of fine, interlacing crystals.

Gypsum also finds some use as a fertilizer, and an artificial calcium sulphate is used as a filling for writing papers.

Bleaching Powder, made by leading chlorine over slaked lime is, as far as its available chlorine is concerned, calcium hypochlorite, but it is probably a mixed salt of the formula $Ca\diagup^{OCl}_{\diagdown Cl}$, being at once chloride and hypochlorite. The bleaching properties of the hypochlorites have already been discussed as due to oxidation by the oxygen which these unstable compounds part with so readily. A solution or paste of bleaching powder and water evolves oxygen gas when heated with the addition of a small amount of a cobalt salt to $70°$–$80°$, the precipitated oxide of cobalt acting as a contact agent. When bleaching powder is treated with an acid, hypochlorous acid, $HClO$, is first formed and then chlorine, as we have seen (p. 114).

Other Compounds of Calcium. — **Calcium Sulphite,** $CaSO_3$, made by passing sulphur dioxide into milk of lime, is used in the manufacture of wood pulp for paper.

Calcium Phosphate. — The insoluble normal phosphate, $Ca_3(PO_4)_2$, in the form of the natural minerals and bone ash, is converted by sulphuric acid into a mixture of acid phosphate, $Ca(H_2PO_4)_2$, and sulphate, $CaSO_4$, which is known as "superphosphate of lime," and employed very largely as a fertilizer.

Calcium Chloride, $CaCl_2$, is a by-product in a number of chemical manufactures. The anhydrous salt is very hygroscopic and is commonly used in laboratories for drying gases and liquids. The salt is usually not completely dehydrated, and as all hydrated substances have a perceptible aqueous tension, gases cannot be completely dried by it. Concentrated sulphuric acid is a better drying agent ; but phosphorous pentoxide is the best, because the metaphosphoric acid, HPO_3, formed with the absorbed water, has no measurable aqueous tension.

Calcium Fluoride, CaF_2, occurs as fluor spar, which is used as the chief source of hydrofluoric acid and other fluorine compounds. It also occurs in small quantities in bones, in the enamel of teeth, and in the ashes of some plants.

Calcium Sulphide, CaS, as often prepared, is luminous in the dark after exposure to light and is the chief constituent of luminous paints. It can be made by heating gypsum with charcoal, or calcium carbonate with sulphur. Its production in the Le Blanc soda process, and the recovery of its sulphur, have been noted in the description of that process.

Calcium Carbide, CaC_2, which is the commercial source of acetylene, is made by heating a mixture of lime and small coal or coke to the high temperature produced in the electric furnace :

$$CaO + 3\ C = CaC_2 + CO.$$
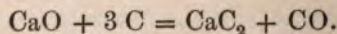
It reacts energetically with water, forming acetylene and slaked lime :

$$CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2.$$
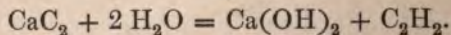
The commercial carbide is impure, and has a grayish color. The impurities occasion the evolution of hydrogen phosphide and other gases.

When nitrogen is passed over the carbide at a white heat, calcium cyanamide, CN.NC, is formed, which decomposes with water gradually, forming ammonia and nitrates. The manufacture of this compound has been begun on a commercial scale as a means of rendering atmospheric nitrogen available for plant life.

Glass is a mixture of silicates. Many silicates are difficult to fuse and crystallize on solidifying, but alkali-calcium and alkali-lead silicates melt rather easily and are usually non-crystalline or amorphous after cooling. We have seen that, in general, the melting point of a mixture is not definite and sharp as in the case of single substances. This is notably the fact with glass, which gradually softens and melts, as its temperature is raised, so that it is impossible to say at what point the transition from solid to liquid occurs. In the plastic state between solid and liquid, glass can be molded, welded, blown into hollow shapes, and given any form which is desired. This fact, together with its transparency and its resistance to chemical agencies, gives it a very wide range of usefulness.

Common glass consists of silicates of calcium and sodium which are produced by melting together limestone, sodium sulphate or carbonate, and quartz sand. Increase in the proportion of silica or limestone makes the glass harder and less fusible, while a larger percentage of alkali has the opposite result. **Plate glass** is made by casting the glass on level iron tables. The sheets are ground to a uniform thickness by sand and

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water and then polished.   **Ordinary window glass** is
prepared by blowing and forming the glass into a hol-
low cylinder, which is then cut lengthwise with a dia-
mond, and slowly unrolled in an oven to a flat sheet.
As in this operation the glass is not heated high enough
to flow freely, its optical properties are irregular, and
objects seen through it are often curiously distorted.
The color of **bottle glass** is due to impurities, chiefly to
iron silicates.   When sodium sulphate is used in making
glass, charcoal or small coal is added to aid the forma-
tion of the silicate by reducing the sulphate :

$$2\,Na_2SO_4 + C + 2\,SiO_2 = 2\,Na_2SiO_3 + CO_2 + 2\,SO_2.$$
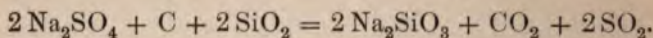
Soda glass is slowly attacked by alkaline and other
solutions, and so for many chemical purposes the more
resistant potash or **Bohemian glass** is employed, made by
substituting potassium for sodium salts.   It softens at
a higher temperature than the soda glass, and the two
are often distinguished as "hard" and "soft" glass,
respectively.

Ordinary glass which has been rapidly cooled is in a
state of tension ; for it is such a poor conductor of heat
that after the surface has become solid, the interior por-
tions are still molten, and, as they cool, their tendency
to contract is opposed by the rigid exterior.   Such glass
is liable to crack when scratched or heated (Prince
Rupert's drops).   All glass articles must therefore be
"annealed" by very gradual cooling.

Flint glass is a soda-lead glass.   It is heavy and has a
high refracting power, and is used for glass ornaments
and for cut glass.

A large number of new glasses have been made of

late years with optical properties which fit them especially for improved microscopic lenses. **Colored glasses** are produced by adding to the usual ingredients certain oxides of metals which form colored silicates. Thus blue may be obtained by cobalt oxide, green by chromium oxide, violet by manganese dioxide, red by metallic copper, gold, or by cuprous oxide, and a fluorescent yellow by uranium oxide. **Milk glass** is made by addition of cryolite and feldspar or bone ash. **Enamels** are easily fusible glasses, usually containing lead and boric acid, or an alkali stannate, and are colored, like glass, with various oxides. For cooking utensils the enamel must be free from lead, and it is usually made from sand, borax, soda, and calcium phosphates or white clay.

Detection of Calcium. — Most compounds of calcium, when moistened with hydrochloric acid, give a dull red flame coloration which shows characteristic bands in the spectroscope. In solutions which contain no other salts except those of the alkalies, calcium may be detected by the precipitation of its sulphate or oxalate.

Quantitative Experiments. — Determination of the hydrogen equivalent of calcium; conversion of calcium, calcium carbonate, or oxide, into chloride, fluoride, hydroxide, or sulphate; determination of carbon monoxide or dioxide from the carbonate. (See *Quantitative Experiments.*)

STRONTIUM AND BARIUM

These two elements, whose compounds in general closely resemble those of calcium, are readily distinguished from it and from each other by their flame colorations and spectra. Their chief natural compounds

are the sulphates and the carbonates. The sulphates, celestine, $SrSO_4$, and heavy spar, $BaSO_4$, are more abundant than the carbonates, strontianite, $SrCO_3$, and witherite, $BaCO_3$. Both are used as sources of the other compounds in the manner described in the introduction to this group. The nitrates of barium and of strontium are used in fireworks to produce green and red fires.

Strontium Hydroxide, $SrOH_2$, is made by slaking the oxide obtained by heating the carbonate or nitrate. It is used in the beet sugar industry to extract the last portion of sugar from molasses. The molasses is the "mother liquor," from which no more sugar can be obtained by crystallization. Strontium hydroxide forms an insoluble compound with sugar from which the molasses can be filtered off. The strontium sucrate is then suspended in water and decomposed by carbon dioxide into sugar, which dissolves in the water, and strontium carbonate which is precipitated. Slaked lime is also used in the same way for recovering the sugar.

Barium Oxides. — Barium oxide, BaO, when heated to about 500° in air or oxygen is converted into barium dioxide, BaO_2. At a higher temperature the reverse change occurs. These reactions are the basis of the Brins process for obtaining oxygen from the air (p. 56). Barium dioxide is used in the manufacture of hydrogen dioxide by the action of dilute acids:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
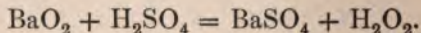
Barium Hydroxide is much more soluble than calcium hydroxide, and its solution, known as baryta water, is used in the laboratory for determining the amount of

carbon dioxide in the air, and for other analytical purposes.

Barium Sulphate. — Finely ground heavy spar, $BaSO_4$, and the precipitated salt are both used in making paint (permanent white), as an adulterant of white lead paint, and as a filler for paper. The insolubility of barium sulphate makes its precipitation a delicate test both for barium and for the sulphuric acid group.

Quantitative Experiments. — Conversion of barium chloride or nitrate into sulphate; chloride into nitrate; sulphate into sulphide; sulphide into chloride; determination of nitrogen in the nitrate. Conversion of strontium nitrate into sulphate. (See *Quantitative Experiments.*)

CHAPTER XXV

MAGNESIUM, ZINC, CADMIUM

THESE three elements resemble each other and form similar compounds. Their chemical activity decreases as their atomic weights increase from magnesium to cadmium, but they do not show the consistent gradation of physical properties which has been noticed in some other groups. While the melting points decrease with increasing atomic weights, and the specific gravity increases, magnesium is very much lighter than the others, and the hardness of zinc is greater than that of magnesium or cadmium. The three metals act only as divalent elements. They are very little changed in air, and act on water at room temperature very slightly or not at all. The oxides of zinc and of cadmium do not form hydroxides with water, but magnesium oxide is slowly changed to a very slightly soluble hydroxide. The hydroxide of zinc is acidic toward strong bases, while the hydroxides of magnesium and cadmium are basic only. All the normal carbonates and phosphates are insoluble in water; the other salts of inorganic acids are soluble. The members of this group give no flame colorations, and do not color the borax bead.

MAGNESIUM

The first compound of this element to attract notice (1695) was the sulphate, which was found in a mineral

spring at Epsom, and on account of its medicinal proper-
ties became widely known as "Epsom salts." Magne-
sium occurs as carbonate alone in magnesite, and as a
double magnesium and calcium carbonate in dolomite;
as silicate in soapstone, in talc, and in meerschaum;
and as a constituent of many compound silicates, such
as asbestos; as sulphate and as double chloride of mag-
nesium and potassium in the Stassfurt deposits (p. 270).
The phosphate is found in small quantities in grains
and in the bones of animals.   Besides these solid
compounds, magnesium sulphate is the chief mineral
constituent of certain spring waters, and the chloride is
present in sea water.

The metal magnesium was first obtained, though not
in a state of purity, by Davy at the time (1807) of his
discovery of sodium and potassium, in the same way
(by electrolysis) that he isolated these metals.   For
some time it was, however, prepared by the action of
sodium on magnesium chloride; but it is now chiefly
obtained by the electrolysis of fused carnallite, which is
the natural double salt of magnesium and potassium.
The demand for the metal is small, but likely to in-
crease on account of its use in making certain useful
alloys with aluminium, which are called "magnalium,"
and as a deoxidizing agent in the metal industries.   It
is sold in stick form or as ribbon or powder.

Properties. — Magnesium is readily kindled and burns
with an intensely bright light which is rich in rays
capable of causing chemical action, and is used on this
account in flash-light photography as well as for signal
lights and in fireworks.   It unites with nitrogen when
heated in this gas, forming the nitride, Mg_3N_2, and con-

sequently the product obtained by burning it in air is a
mixture of oxide and nitride.   The nitride is formed
more abundantly when the magnesium is burned with-
out free access of air, as in a partly covered crucible.
The presence of the nitride is easily shown, for it reacts
with water to form ammonia :

$$Mg_3N_2 + 6\,H_2O = 3\,Mg(OH)_2 + 2\,NH_3.$$
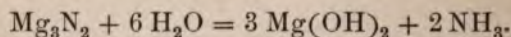
Magnesium evolves hydrogen slowly from boiling water,
and burns brilliantly when heated in steam (p. 35).
Burning magnesium continues to burn in carbon diox-
ide, with separation of carbon, and it reduces the oxides
of boron, of silicon, and of many metals, setting these
elements free.   Hence, when magnesium is burned in
contact with glass or porcelain black stains are produced.

Magnesium Oxide, MgO, is made commercially by
heating the carbonate, and is known as "calcined mag-
nesia."   It can also be prepared from the hydroxide or
nitrate, or by burning the metal.   It is more infusible
than lime and is used as a refractory lining for furnaces
and for making crucibles.   When made from the nitrate
or natural carbonate at a low temperature, it sets like
lime with water; but most varieties do not have this
property, though they unite with water to form the
hydroxide.   The hydroxide, $Mg(OH)_2$, is precipitated
from solutions of magnesium salts by sodium or potas-
sium hydroxides, but ammonia does not precipitate it
in the presence of ammonium salts.   This behavior
with ammonia and its salts is explained by the ionic
theory as due to the fact that the ammonium hydroxide
is only slightly dissociated, while the dissociation of the
ammonium salts is large.   The presence of the NH_4 ions

from the salts renders the dissociation of the hydroxide so small that OH′ ions are not available for the formation of the magnesium hydroxide. (*Cf.* p. 258). Magnesium hydroxide is very slightly soluble, but when moistened gives an alkaline reaction.

Magnesium Carbonates. — The normal carbonate $MgCO_3$ occurs as magnesite, but the precipitate formed on adding an alkaline carbonate to magnesium solutions consists of hydrated basic carbonates of variable composition. The carbonates made in this way are known as "magnesia alba." Magnesium carbonate dissolves in solutions of ammonium salts and hence is not precipitated completely by ammonium carbonate, and not at all in the presence of ammonium chloride. Magnesium carbonates are soluble in carbonic acid with the formation of acid carbonates, as in the case of calcium carbonate, and hence are found in natural waters, making part of the temporary hardness.

Magnesium Sulphate, in the natural form of kieserite, $MgSO_4, H_2O$, dissolves in water very slowly, being gradually converted into the soluble hydrate $MgSO_4, 7 H_2O$. The supply of this salt was formerly obtained by treating magnesite or dolomite with sulphuric acid, but it is now derived from the kieserite which occurs abundantly in the Stassfurt deposits (p. 270). It finds a number of industrial uses, and is used in medicine under the old name of Epsom salts. Magnesium sulphate forms a number of hydrates, the usual one being the heptahydrate, $MgSO_4, 7 H_2O$, analogous to the white and green vitriols.

Magnesium Chloride, $MgCl_2$, is obtained chiefly from the double chloride of potassium and magnesium, which

occurs as carnallite at Stassfurt. It crystallizes as $MgCl_2, 6H_2O$. The anhydrous salt cannot be made pure by heating, for hydrolysis takes place, and part of the chloride is converted into oxide:

$$MgCl_2 + H_2O = MgO + 2HCl.$$
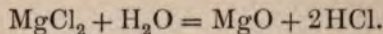
On adding ammonium chloride to the solution of magnesium chloride, the double salt which is obtained by evaporation can be deprived of its water without hydrolysis taking place, and then, on further heating, the anhydrous magnesium chloride is left.

The substitution of magnesium oxide for lime in the Solvay soda process has been proposed. By its use, the chlorine which goes to waste in calcium chloride could be converted into hydrochloric acid by the reaction given above, while the magnesium oxide would be regenerated at the same time. On account of the hydrochloric acid produced by the hydrolysis of magnesium chloride in strong solutions, water containing this salt corrodes metals, and hence sea water cannot be used in ships' boilers.

Detection of Magnesium. — The double phosphate of ammonium and magnesium, $(NH_4)MgPO_4, 6H_2O$, is quite insoluble in water containing ammonia, and serves as a means of detecting the presence of magnesium in solution, and for its quantitative determination. Solid compounds of magnesium when ignited before the blowpipe yield an infusible mass which, when moistened with cobalt nitrate and again ignited, assumes a pale rose color.

Quantitative Experiments. — Determination of the hydrogen equivalent; conversion of magnesium into oxide

or sulphate; of the carbonate into oxide. (See *Quantitative Experiments.*)

ZINC

Properties. — Zinc is one of the familiar metals in common use, and we have already had occasion to learn some of its properties. Polished zinc has a bluish white color. It tarnishes slowly in the air with the formation of a film of basic carbonate which protects the metal from further corrosion. When cold, zinc is somewhat brittle, but between 100° and 150° it is malleable and ductile. At about 200° it is so brittle that it may be powdered in a mortar. It melts at 419°, and boils at about 920°. Its vapor burns brilliantly, forming a white smoke of oxide. Heated zinc decomposes steam with evolution of hydrogen. The action of acids on zinc has been discussed (pp. 90, 139). Solutions of alkalies also dissolve zinc with evolution of hydrogen and the formation of zincates:

$$Zn + 2\,NaOH = Na_2ZnO_2 + H_2.$$
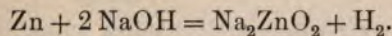
For laboratory purposes zinc is usually employed in leafy form produced by dropping melted zinc from a height of three or four feet into water. In this form it presents a greater surface and consequently acts more rapidly. Still more efficient as a reducing agent is zinc dust, a mixture of very fine zinc and zinc oxide which is obtained in the process of reducing the metal from its ores. Sheet zinc is used for many purposes. The metal is also employed in batteries, for "galvanizing" iron (p. 334), and for making brass and other alloys. Commercial zinc is seldom pure. The purer it is, the less is it attacked by dilute sulphuric acid (p. 90).

Occurrence and Extraction of Zinc. — The ores of zinc are the oxide (zincite), oxide of zinc, iron, and manganese (franklinite), carbonate (calamine), sulphide (blende), and silicate.   The oxide of zinc is reduced by heating in earthenware retorts with coal.   The carbonate, sulphide, and silicate are first changed to oxide by roasting, the silicate with the addition of lime to combine with the silica, and then reduced by carbon.   The zinc comes off as vapor and is condensed in receivers:

$$ZnO + C = Zn + CO.$$
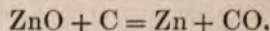
At first, before the receiver becomes heated, the vapors of zinc condense immediately to the solid state in the form of "zinc dust," which contains some oxide, and later, liquid zinc is produced.   The molten zinc is cast in blocks and is called "spelter."   The crude zinc contains small amounts of lead and cadmium, and often arsenic, from the presence of these elements in the ores.

Zinc is purified by distillation, or pure zinc may be obtained from purified compounds by reduction or electrolysis.

Compounds of Zinc. — Natural **zinc oxide**, ZnO, is red from the presence of manganese compounds.   The artificial zinc oxide is white when cool, and yellow when hot.   It is made in large quantities by burning zinc vapor, either from boiling zinc, or as it comes from the reduction of the ores.   It is used for making paint, which has the advantage over white lead paint of not being darkened by hydrogen sulphide, since zinc sulphide is white, and of not being poisonous.   Zinc oxide is reduced by hydrogen with difficulty.

Zinc Hydroxide, $Zn(OH)_2$, acts as a feeble acid towards strong bases with the formation of zincates:

$$Zn(OH)_2 + 2\,NaOH \rightleftharpoons Zn(ONa)_2 + 2\,H_2O.$$
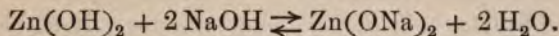
The zincate is soluble, and hence zinc hydroxide precipitated by an alkali dissolves in an excess of the reagent. But a considerable excess is necessary, because the action is reversible. If ammonium hydroxide is used, the zinc hydroxide forms soluble compounds containing complex groups in which zinc replaces part of the hydrogen in ammonium.

Zinc Sulphate, $ZnSO_4$, is the most important of all the salts of zinc. In its crystalline form it is $ZnSO_4.7\,H_2O$, which is known as "white vitriol." It is obtained commercially by roasting blende. The sulphate is dissolved in water and crystallized from the solution. The anhydrous salt is obtained by heating, and is decomposed only at red heat.

Zinc Chloride, $ZnCl_2$, is a very deliquescent substance. It withdraws the elements of water from some organic substances and is used for that purpose in the laboratory. Like magnesium chloride, it is hydrolyzed to some extent in solution and hence has an acid reaction. On evaporating to dryness, hydrogen chloride is given off and some basic chloride is formed:

$$ZnCl_2 + H_2O = Zn(OH)Cl + HCl.$$
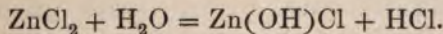
Zinc chloride has marked antiseptic properties and is used for preventing the decay of wood. Its solution is also employed as a soldering fluid, as it cleans the metal surfaces by dissolving any oxide which is present.

A concentrated solution dissolves much zinc oxide and solidifies to a hard mass of oxychloride. This is used as a cement by dentists.

Zinc Sulphide, ZnS, which occurs naturally as blende, is obtained as a white precipitate by hydrogen sulphide in alkaline solutions, or by the addition of ammonium sulphide. It is insoluble in dilute acetic acid. It is not reduced when heated in hydrogen, and may be prepared in this way for weighing as a means of determining zinc in its compounds. When precipitated zinc sulphide containing small amounts of alkali chlorides and sulphides of other metals, such as bismuth, copper, or manganese, is heated to a white heat in a covered crucible, it becomes luminous after exposure to light, and also when exposed to X rays or the radium radiations. Perfectly pure sulphide of zinc does not possess this property.

Zinc Carbonates. — The normal carbonate occurs as calamine and can be precipitated from zinc solutions by sodium bicarbonate:

$$ZnSO_4 + 2NaHCO_3 = ZnCO_3 + Na_2SO_4 + H_2O + CO_2,$$
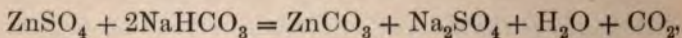
but changes easily into basic carbonates; and if normal alkaline carbonate is used to precipitate zinc solutions, basic carbonates are at once formed as in the case of magnesium.

Detection of Zinc. — Solid compounds of zinc, moistened with cobalt nitrate and strongly heated, give an infusible green mass. A characteristic precipitate from zinc solutions is the white sulphide which is soluble in inorganic acids but insoluble in dilute acetic acid.

Quantitative Experiments. — Determination of the hydrogen equivalent; conversion of zinc into oxide,

chloride, or sulphate; of the oxide, sulphide, or carbonate
into chloride or sulphate; of the carbonate into oxide;
and of the sulphate into sulphide. (See *Quantitative
Experiments.*)

CADMIUM

This metal was discovered in 1817 in a pharmaceutical
preparation of zinc oxide which was suspected of con-
taining arsenic because of the yellow precipitate which
its solution gave with hydrogen sulphide. Cadmium
occurs chiefly as sulphide in greenockite, and it accom-
panies zinc in many of its ores. Having a lower boiling
point than zinc, it is found in the first portions of zinc
dust which are obtained in the extraction of this metal.
It may be purified from zinc by repeated distillation.

Cadmium resembles zinc and forms similar compounds.
It is acted on by hydrochloric and sulphuric acids much
more slowly than is zinc, but dissolves readily in nitric
acid. Its **oxide**, CdO, is brown. It is readily reduced
by hydrogen. The **sulphide**, CdS, unlike that of zinc,
is precipitated from acid solutions, and in this way, as
well as by its yellow color, serves to distinguish the two
metals in solutions of their salts. Its salts are not hy-
drolyzed like those of zinc. The metal is used in certain
fusible alloys and in making standard cells for electro-
motive force, and its sulphide is employed as a yellow
pigment, "cadmium yellow."

Quantitative Experiments. — Determination of the
hydrogen equivalent; conversion of cadmium into oxide,
chloride, or sulphate; of the oxide into cadmium, or into
the chloride or sulphide; of the sulphide into chloride;
and of the chloride into sulphate. (See *Quantitative
Experiments.*)

CHAPTER XXVI

ALUMINIUM

ALUMINIUM is the most abundant of the metallic elements, and its amount in nature is exceeded only by that of two non-metals, oxygen and silicon. It is found only in compounds; in largest amount in numerous silicates of which the most important are the double silicates of aluminium and potassium or sodium, known as common and soda feldspars. The feldspars occur by themselves and are also constituents of granite and of many other rocks. By the weathering of feldspar, kaolin, or porcelain clay, is formed; and the common clays are the result of the disintegration of the feldspathic rocks. Among the other silicates are the garnets and micas. Cryolite, already mentioned (p. 255), contains aluminium with sodium as a double fluoride. As oxide, aluminium occurs as corundum, of which the ruby and sapphire are varieties and emery is an impure form. The hydroxides, diaspore and bauxite, are found in considerable quantity. While compounds of aluminium are found in all soils, they are taken up by plants in very small amount and are not necessary for their development.

The sources for the preparation of aluminium compounds are various. Of the first importance is kaolin, the purest natural silicate, and bauxite, an hydroxide. Cryolite is also employed, and to some extent alum

shale and alum stone, a natural double sulphate of aluminium and potassium. Kaolin is converted into sulphate by the action of strong sulphuric acid, and the sulphate is also obtained from alum stone and from alum shales by roasting and exposure to the weather. Bauxite is converted into sulphate by sulphuric acid, or into sodium aluminate by heating with a strong solution of caustic soda under pressure. Cryolite heated with calcium carbonate also yields sodium aluminate (p. 265). From the aluminate, the hydroxide is precipitated by carbon dioxide.

Extraction. — Aluminium oxide is not reduced by carbon or hydrogen. Davy failed to obtain the metal by the electrolytic method which was so successful with the alkalies and alkaline earths, and it was first prepared by Wöhler in 1827 by the action of potassium on its chloride. Aluminium is now made on a commercial scale from the oxide dissolved in fused cryolite, by electrolysis with a powerful electric current. It is important that the oxide be as pure as possible, and special methods are employed for the preparation of suitable material from bauxite and other sources.

Properties. — Aluminium is white and lustrous, and does not tarnish in the air. It is much lighter than any other metal commonly used, being but little more than one third as heavy as iron. It is hard, very malleable, and ductile, though at a temperature somewhat below its melting point it can be powdered. It is an excellent conductor of electricity, being better than copper when the two are compared, not by size of the wire, but by weight. It does not work well in the lathe and is difficult to solder.

x

Although aluminium remains almost unchanged in air, this is because a closely adherent film of transparent oxide is immediately formed on the exposed surface, which protects it from further action. When the surface is amalgamated with mercury by rubbing it with mercuric chloride, the aluminium dissolved in mercury can no longer form a continuous film of oxide, and a mosslike growth of hydroxide immediately appears. The activity of aluminium towards oxygen is so great that a mixture of the powdered metal and iron oxide may be ignited by a fuse of magnesium ribbon, with the result that molten iron is produced, the temperature reaching 3000°. Most other metals may be similarly reduced; and this method, developed by Goldschmidt, and called the Goldschmidt or "Thermite" process, is employed for obtaining metals, like chromium, whose reduction in any other way is difficult, as well as for welding iron and steel rails, etc.

Finely divided aluminium burns brilliantly when heated in air or steam. The metal dissolves readily in hydrochloric acid. With hot concentrated sulphuric acid it gives sulphur dioxide. Dilute sulphuric acid and dilute nitric acid act very slowly. With boiling solutions of the alkalies it gives hydrogen with the formation of aluminates:

$$2\,Al + 6\,NaOH = 2\,Na_3AlO_3 + 3\,H_2.$$
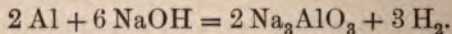
Although aluminium is somewhat attacked by most salt solutions and organic acids, it is largely used for cooking utensils, because of its lightness and other good qualities. Aluminium is also used for making small articles; in the form of thin leaf for lettering book

covers and signs, and as powder for aluminium paint. It is a constituent of several useful alloys, such as magnalium and aluminium bronze. Probably most of the aluminium manufactured is used in the iron and steel industries. A small addition of aluminium frees the molten metal from oxide and makes it more liquid, and thus less liable to retain bubbles of gas. Its use as wire for conducting electric currents is of growing importance. Aluminium is always trivalent.

ALUMINIUM COMPOUNDS

Aluminium Sulphate, $Al_2(SO_4)_3$, is much the most important single salt of aluminium. The methods of obtaining it have been already given. It forms a finely crystallizing double salt with potassium sulphate. This salt, known as **alum,** $KAl(SO_4)_2, 12\ H_2O$, has been known and used much longer than any other salt of aluminium. For practical uses, in most of which the hydroxide is required, the simple sulphate is preferable, and has largely displaced alum under the name of " concentrated alum." While potassium alum was the original salt of this name (from which the name of aluminium is derived) there is a considerable group of similar salts which are known as **the alums.** They are all double sulphates of a trivalent and a monovalent metal. They all crystallize with the same amount of water, and are isomorphous, growing in each other's solutions. The place of potassium may be taken by any alkali metal except lithium, or by the ammonium group, or silver; that of aluminium, by chromium, iron, or manganese.

Aluminium sulphate and alum are used in dyeing, and for numerous other purposes, such as sizing paper, fire-

proofing cloth, hardening plaster; and alum is used in medicine as an astringent.

Alum solutions all have an acid reaction because of hydrolysis which gives some free acid. On adding an alkali to an alum solution and stirring, the hydroxide at first precipitated is dissolved, until the solution becomes neutral to test paper. It now contains a basic salt and is used as a mordant under the name of "neutral alum."

Aluminium Chloride, $AlCl_3$, $6H_2O$, is readily decomposed on heating, leaving the oxide. The anhydrous chloride may be made by the action of chlorine on aluminium, or by heating the oxide with charcoal in chlorine. It sublimes without melting and fumes in moist air because of the formation of hydrogen chloride by hydrolysis with the moisture. It is an important agent in the synthesis of organic compounds.

Aluminium Hydroxide. — On adding an alkaline hydroxide to aluminium solutions, a gelatinous precipitate is formed which consists of a hydrated aluminium hydroxide. The hydroxide having the composition $Al(OH)_3$ is not easily obtained, as on heating the precipitated substance it loses water continuously with the final formation of the oxide, Al_2O_3. The hydroxide, $Al(OH)_3$, may, however, be assumed to be present in the hydrated precipitate. The natural oxides, and the artificial oxide after strong heating, are insoluble in acids.

The hydroxide acts both as a weak base and as a weak acid. It dissolves readily in an excess of the hydroxides of potassium and sodium to form aluminates:

$$Al(OH)_3 + 3\,NaOH \rightleftarrows Na_3AlO_3 + 3\,H_2O\,;$$
$$Al(OH)_3 + NaOH \rightleftarrows NaAlO_2 + 2\,H_2O.$$
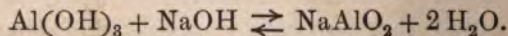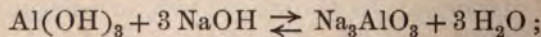
Since the reactions are reversible, an excess of sodium hydroxide is required for complete solution. If carbon dioxide is led into the solution, the hydroxide is precipitated (*cf.* p. 265). No carbonate of aluminium is stable, and hence the hydroxide is precipitated when an alkaline carbonate is added to aluminium solutions:

$$2\,AlCl_3 + 3\,Na_2CO_3 + 3\,H_2O$$
$$= 6\,NaCl + 2\,Al(OH)_3 + 3\,CO_2.$$
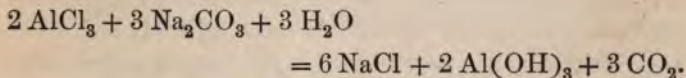
The hydroxide precipitated by ammonia is insoluble in excess of this reagent. From aluminium hydroxide, $Al(OH)_3$, which, from its weakly acidic character, may be called orthoaluminic acid, other acids may be theoretically derived by the loss of the elements of water, as in the case of the phosphoric acids. We would thus have, besides the ortho-acid, such compounds as H_4AlO_5 and $HAlO_2$, corresponding to the pyro- and meta-phosphoric acids. These are, in fact, found in mineral forms; and several other minerals, such as spinelle, $Mg(AlO_2)_2$, are metaluminates. The soluble metaluminate of sodium, $NaAlO_2$, appears in one of the above equations, and the metaluminate of calcium, $Ca(AlO_2)_2$, is precipitated by it from calcium solutions.

Aluminium Sulphide, Al_2S_3, can be made by heating aluminium and sulphur. It is completely hydrolyzed by water, and hence the hydroxide, instead of the sulphide, is precipitated by ammonium sulphide from solutions of aluminium salts.

Dyeing ; Mordants. — Aluminium hydroxide is a gelatinous substance which has the property of uniting with many substances with the formation of insoluble

compounds.   On this property depends the use of
aluminium salts in clarifying water and in dyeing.
Many dyes will not unite directly with cloth fibers to
form fast colors.   This is especially the case with
cotton and linen.   If, however, the fabric is first
treated with a salt of aluminium, the hydroxide, which
is present through hydrolysis, is separated from the
solution and unites firmly with the fibers; and when
the cloth thus prepared is brought into a solution of
the dye, the dye combines with the hydroxide to form a
fast color.   A substance which serves in this way to
fix the dye in the cloth is called a **mordant**.   Many
compounds of metals act as mordants, and the color or
shade produced by a given dye depends partly on the
mordant, since in each case differently colored com-
pounds are formed.   The colored compounds are
called lakes, and are used by themselves as pigments
in painting.

Aluminium Silicates; Pottery. — The clays are more
or less impure hydrated silicates of aluminium, which
have been formed from the decomposition of feldspathic
rocks.   The plasticity of wet clay and the hardness,
strength, and chemical resistance which objects made
from it acquire, after being strongly heated, have led to
its use for bricks and pottery from the earliest times.

Kaolin is the purest natural silicate of aluminium.
It is infusible and hence does not gain coherence and
strength by being heated.   If, however, some fusible
material, such as feldspar, is mixed with it, this melts
on firing and binds the clay together into a hard mass,
which is translucent, if enough of the flux is added.
The making of porcelain depends on this.   The less

pure clays which are used for earthenware, bricks, etc., contain substances already mixed with the aluminium silicates, which make the addition of a flux unnecessary. These impurities are also the occasion of a color,— the common red being due to the presence of iron compounds. Battery jars, flower pots, bricks, etc., are porous, as are most of the pottery products, after the first firing. For many purposes this is objectionable, and the surfaces are rendered non-porous by a glaze. This is produced by applying to the surface some materials which melt at a high temperature to a closely adherent film, or which, like lead oxide, form fusible silicates with the clay.

Ultramarine is a double silicate of aluminium and sodium, containing some sulphur. It was formerly obtained by grinding the blue mineral lapis lazuli, but is now made more cheaply and in a variety of colors by heating kaolin, sodium carbonate, sulphur, and charcoal. It is largely used as a pigment.

Detection of Aluminium. — Solid compounds of aluminium when moistened with cobalt nitrate and strongly ignited give a blue mass. The precipitation and behavior of the hydroxide distinguishes aluminium in solutions.

Quantitative Experiments. — Determination of the hydrogen equivalent ; conversion of aluminium into oxide or sulphate. (See *Quantitative Experiments.*)

CHAPTER XXVII

CHROMIUM AND MANGANESE

CHROMIUM

In 1797 the investigation of a new mineral resulted in the discovery that it contained a previously unknown element in combination with lead and oxygen. This element was named chromium because its compounds are usually colored. Chromium does not occur free, and its compounds are not very abundant or widely distributed. The most important mineral which contains it is chrome iron stone, an oxide of chromium and iron; and this is the usual source of chromium compounds. Chromium is found in a few other minerals, such as the lead chromate in which it was discovered, and traces of its compounds form the coloring matter of certain green minerals, such as the emerald.

Chromium. — Chromium can be reduced from its oxide by carbon, but only at a very high temperature. It may, however, be readily prepared by reduction with aluminium by the thermite process. An alloy of chromium and iron is made commercially by the reduction of chrome iron stone by coke in the electric furnace, and is used in making chrome steel. Chromium resembles iron in appearance, but is much harder, much less fusible, and less easily attacked by acids. It forms three

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oxides, in which its valence is two, three, and six, respectively. The first of these oxides is basic only and forms the chromous salts; the second is basic, forming chromic salts, and also acidic with the formation of chromites; while the third is wholly acidic and gives chromic acid and the chromates.

The Chromates. — When powdered chrome iron stone is heated with saltpeter, a mass is obtained from which water dissolves a yellow salt, leaving insoluble iron oxide. In the technical treatment of the chromium ore a mixture of potash and limestone is used instead of the more expensive saltpeter, and the operation is conducted with free access of air for the sake of oxidation. By using a solution of potassium sulphate for the extraction of the mass, any calcium chromate which has been formed is changed into potassium chromate with precipitation of the nearly insoluble calcium sulphate. From the solution pale yellow **potassium chromate,** K_2CrO_4, is obtained. As this is very soluble in water and hence difficult to purify, sulphuric acid is usually added to the solution to convert it into the orange-colored **dichromate,** $K_2Cr_2O_7$, which is much less soluble in cold than in hot water, and is easily purified by crystallization. The sodium chromates are made in a similar manner. They are cheaper and are largely used on this account and because of their greater solubility. The chromates of the alkalies and of ammonium are the most soluble chromates, and insoluble yellow or red chromates of other metals are precipitated from their solutions by the alkaline chromates.

Chromates and Dichromates. — Potassium (or sodium) chromate is changed into the dichromate when an acid

is added to its solution, the reaction being indicated by the change in color from yellow to orange.   We should expect the formation of an acid chromate, $KHCrO_4$, under these conditions :

$$K_2CrO_4 + 2\,HCl = 2\,KCl + H_2CrO_4;$$
and $$K_2CrO_4 + H_2CrO_4 = 2\,KHCrO_4;$$
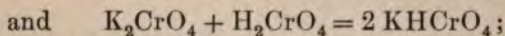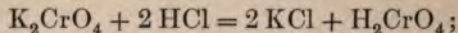
but the acid salt is evidently too unstable to exist, and so the dichromate is formed instead :

$$2\,KHCrO_4 = K_2Cr_2O_7 + H_2O.$$
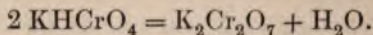
Acid potassium sulphate undergoes a similar change, when the dry salt is heated :

$$2\,KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O;$$
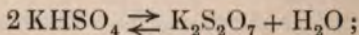
but this gives the acid sulphate again when dissolved in water.   The reaction with the chromate is not reversible. It is brought about by the weakest acid.   On adding an alkali to a dichromate solution, the color changes back to that of the yellow chromate :

$$K_2Cr_2O_7 + 2\,KOH = 2\,K_2CrO_4 + H_2O.$$
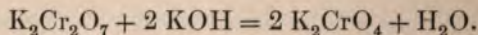
When not in solution, potassium chromate is an entirely stable compound ; and the dichromate decomposes only at a white heat, yielding oxygen, the chromate, and chromic oxide :

$$4\,K_2Cr_2O_7 = 4\,K_2CrO_4 + 2\,Cr_2O_3 + 3\,O_2.$$
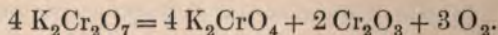
Acid solutions of chromates (dichromates) are powerful oxidizing agents, and are themselves reduced with a striking change of color to a dark green, which is charac-

teristic of the chromic salts. For instance, with sulphurous acid:

$$K_2Cr_2O_7 + H_2SO_4 + 3 H_2SO_3$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 4 H_2O ;$$
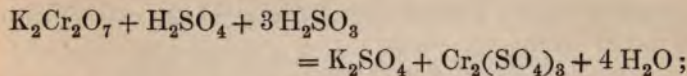
with hydrochloric acid, chlorine is set free:

$$K_2Cr_2O_7 + 14 HCl = 2 KCl + 2 CrCl_3 + 7 H_2O + 3 Cl_2.$$
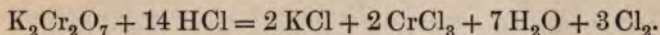
The dichromates find many uses as oxidizing agents. The oxidizing effect which a given weight of the salt can produce is calculated from the equation :

$$K_2Cr_2O_7 + 4 H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4 H_2O + 3 O;$$
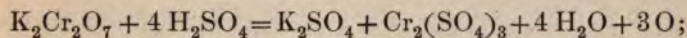
which shows that three atomic weights of oxygen are supplied by each molecular weight of the dichromate. Oxidations of active reducing agents occur with the neutral salt, and organic matter is oxidized by it on exposure to light. A gelatine film to which potassium dichromate has been added is rendered insoluble by the action of light, and this is made the basis for certain photographic printing processes.

The dichromates of potassium and sodium are the immediate sources of other chromium compounds, and are themselves used in the dyeing and tanning industries.

The chromates are analogous to the sulphates in their formulas, and the salts show also a general correspondence in their relative solubilities.

Lead Chromate, $PbCrO_4$, is used as a yellow pigment, "chrome yellow." A basic chromate, $(Pb_2O)CrO_4$, is "chrome red." Cloth may be dyed yellow by using a lead salt as a mordant and then dipping the cloth into a solution of potassium or sodium chromate.

Ammonium Dichromate, $(NH_4)_2Cr_2O_7$, like other ammonium salts, decomposes when heated, all of its hydrogen uniting with oxygen to form water:

$$(NH_4)_2Cr_2O_7 = 4\,H_2O + N_2 + Cr_2O_3.$$
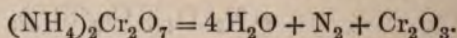
The decomposition begins when the salt is slightly heated, and goes on of itself with the appearance of burning.   Nitrogen and steam are evolved, and a voluminous dark green powder of chromic oxide remains.

Chromic Anhydride, CrO_3. — When concentrated sulphuric acid is added in sufficient amount to a saturated solution of a dichromate, red crystals separate which have the composition CrO_3.   This is the anhydride of the unstable chromic acid, H_2CrO_4, which corresponds to the chromates.   It is analogous to sulphuric anhydride, as chromic acid and the chromates are to sulphuric acid and the sulphates, and the dichromates to the pyrosulphates.

Chromic anhydride is rather unstable, losing oxygen when heated and changing into the green chromic oxide:

$$4\,CrO_3 = 2\,Cr_2O_3 + 3\,O_2.$$
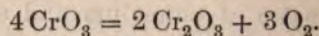
It is a very powerful oxidizing agent, kindling strong alcohol when this is dropped on to it.   In solution it gives either chromic acid, H_2CrO_4, or dichromic acid, $H_2Cr_2O_7$, both of which are very unstable.   An acid solution of a dichromate may be considered to owe its oxidizing power to the presence of this substance:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2Cr_2O_7;$$

and
$$H_2Cr_2O_7 = H_2O + 2\,CrO_3.$$
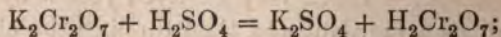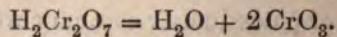
Chromic Oxide and Hydroxide. — From the green solutions obtained by the reduction of chromates, the alkalies precipitate a gelatinous, bluish green, hydrated hydroxide of chromium, $Cr(OH)_3$, which is converted into chromic oxide, Cr_2O_3, when separated from the solution and heated. The precipitate is dissolved by acids, giving **chromic salts**. It is also soluble in an excess of potassium or sodium hydroxide, indicating that the hydroxide has acid properties towards strong bases. On boiling the alkaline solution, the chromium hydroxide is again precipitated. Aluminium hydroxide is similarly dissolved by an excess of alkali, but is not reprecipitated by boiling the solution. This furnishes a means of separating chromium from aluminium.

Chromic oxide, after ignition, is insoluble in acids. It may be converted into soluble compounds by fusion with acid potassium sulphate or with saltpeter. It is used in making green paint.

Chromites. — The solution formed by dissolving chromic hydroxide in an alkali contains an alkaline chromite, $NaCrO_2$, corresponding to partly dehydrated chromic hydroxide:

$$Cr(OH)_3 - H_2O = HCrO_2,$$
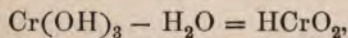
which acts as an acid. Some insoluble chromites occur as minerals, chromic iron stone being a chromite of iron, $Fe(CrO_2)_2$. The acid character of chromic hydroxide is very feeble.

Chromic Salts. — These salts may be made by the action of acids on chromic hydroxide. Their solutions undergo curious changes in color due to hydrolysis. The anhydrous **chloride**, $CrCl_3$, is obtained by heating a

mixture of chromic oxide and carbon in a current of chlorine.   The chloride sublimes, forming reddish violet scales.   The **sulphate** is an alum-forming sulphate.   It crystallizes from solutions of potassium dichromate and sulphuric acid, which have been used for oxidation, as a dark reddish salt, $KCr(SO_4)_2,12\,H_2O$.   It is used as a mordant in dyeing.

Chromous Compounds. — By heating chromium in hydrogen chloride, or chromic chloride in hydrogen, white crystals of **chromous chloride**, $CrCl_2$, are produced. This salt forms a blue solution which is a powerful reducing agent, and absorbs oxygen gas very readily, being itself oxidized to basic chromic salts.   A solution of chromous chloride, made by reducing potassium dichromate in the presence of strong hydrochloric acid, is used as a reducing agent, and in gas analysis for removing oxygen from other gases.   **Chromous hydroxide**, $Cr(OH)_2$, is precipitated from chromous chloride solutions by alkalies.   It is a yellow substance which oxidizes very readily, and when heated gives chromic oxide, water, and hydrogen:

$$2\,Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$
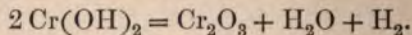
Chromous Sulphate, $CrSO_4,7\,H_2O$, is formed by the action of sulphuric acid on chromous chloride or on chromium.   Its solution gives blue crystals, isomorphous with zinc sulphate.

Detection of Chromium. — Chromium compounds all impart an emerald-green color to the borax bead.   When fused with saltpeter and soda they form a yellow mass of chromate which, after treatment with acetic acid to destroy the excess of carbonate, precipitates yellow lead *chrom*ate from solutions of lead salts.

Quantitative Experiments. — Conversion of chromic oxide into sulphate; determination of chromic oxide, and of nitrogen in ammonium dichromate. (See *Quantitative Experiments*.)

MANGANESE

Although the chief ore of this metal, pyrolusite, had been known and used in glass making for a very long time, it was not until 1774 that it was recognized that it contained a new element.

Pyrolusite is manganese dioxide, MnO_2, which is largely used in making chlorine, and serves as the principal source of the metal and its compounds. Manganese occurs less abundantly in other oxides, and as carbonate and sulphide. It also is a constituent, in small quantities, of many other minerals.

Manganese. — Manganese oxides are reduced by carbon only at the very highest temperatures; the metal is, however, obtained readily by the thermite process in which the oxides are reduced by aluminium. Alloys of manganese and iron are obtained without difficulty in blast furnaces from ores which contain these two metals, and are much used in making steel. Manganese has the appearance of cast iron. It is harder and heavier than iron, and oxidizes more readily. It dissolves easily in dilute acids and evolves hydrogen from boiling water. The pure metal finds no practical use, but several of its alloys are of importance, especially those containing iron.

Oxides. — **Manganese dioxide,** MnO_2, seldom occurs entirely pure in the mineral pyrolusite. The pure oxide may be made from manganous nitrate by prolonged gentle heating, and precipitates having nearly the composition of the dioxide are formed in a number of

reactions.   When the dioxide is strongly heated it loses part of its oxygen and is changed into **mangano-manganic oxide**, Mn_3O_4:

$$3 MnO_2 = Mn_3O_4 + O_2.$$
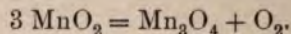
Heated in hydrogen, both of these oxides are reduced to **manganous oxide**, MnO.   A fourth oxide, **manganic oxide**, Mn_2O_3, is obtained by igniting any of the other oxides in oxygen, and is changed to Mn_3O_4 when heated in air, or to MnO in hydrogen.   Thus the final result of heating any of these oxides in air is Mn_3O_4; in hydrogen, MnO; and in oxygen, Mn_2O_3.   Two more very unstable oxides of manganese are known : **manganese trioxide**, MnO_3, and **manganese heptoxide**, Mn_2O_7.   They are both acid anhydrides.

When any of these oxides is acted upon by an acid, salts of manganese are obtained of the type of $MnCl_2$. In these the manganese is a dyad and the corresponding basic oxide is MnO.   With this oxide, acids give the salts and water; with the other oxides, oxygen is also formed, and is either set free or oxidizes the acid as in the reaction for making chlorine from hydrochloric acid and manganese dioxide.

Besides its employment for making chlorine and manganese compounds, manganese dioxide is used in glass making to decolorize the greenish glass which results from iron in the sand from which the glass is made. The dioxide oxidizes the green ferrous silicate to pale yellow ferric silicate, and this color is neutralized by the amethyst color which manganese compounds impart to glass.

Manganous oxide, MnO, is a green powder; mangano-

manganic oxide, Mn_3O_4, is red; manganic oxide, Mn_3O_4, is brown; and the dioxide, MnO_2, is black.

Manganous Hydroxide, $Mn(OH)_2$, is formed as a white precipitate when alkalies are added to solutions of manganous salts, but quickly darkens from oxidation in the air. This ready oxidation of the hydroxide by air is utilized in the soda industry for the regeneration of the higher oxides of manganese which are used for making chlorine (p. 264).

Valence of Manganese. —It appears from the formulas for the manganese oxides that the element has several valences. In MnO the valence is two; in MnO_2, four; in MnO_3, six; and in Mn_2O_7, seven. The oxide, Mn_3O_4, when treated with dilute acids gives manganous salts, in which the manganese is a dyad, with separation of MnO_2, and hence it may be regarded as a manganese salt of the hydrated dioxide, $Mn(OH)_4$, in which the hydrogen is replaced by dyad manganese : $Mn_2(MnO_4)$. It thus contains both dyad and tetrad manganese. The reaction with dilute acids is ;

$$Mn_2(MnO_4) + 4\ HNO_3 = 2\ Mn(NO_3)_2 + 2\ H_2O + MnO_2.$$
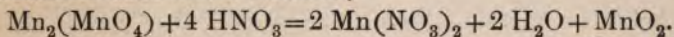
In Mn_2O_3 manganese may be a triad, as in $\begin{matrix} Mn \diagup O \\ \diagdown O \\ Mn \diagdown O \end{matrix}$ O (and

there are some salts of triad-manganese), or both dyad and tetrad as in $Mn(MnO_3)$ which corresponds to $MnO(OH)_2$ from $Mn(OH)_4 - H_2O$; since like Mn_3O_4 it gives MnO_2 with dilute acids. Manganese is thus seen to be unusual in the number of valences which it shows.

But, although manganese forms many classes of compounds, only a few of them are stable enough to be of individual importance. These are the manganous salts,

Y

in which manganese is a dyad, manganese dioxide, in which it is a tetrad, and potassium and sodium permanganates, in which it is a heptad.

Salts of Manganese. — Some unstable salts of triad manganese corresponding to manganic oxide, Mn_3O_4, are known, the most stable being a cæsium-manganese alum, $CsMn(SO_4)_2, 12 H_2O$. These are the **manganic salts**. The only stable salts of manganese, in which it is united with acid radicals, are those of dyad manganese, and correspond to the manganous oxide, MnO. As has been stated, they are obtained by the action of acids on any of the oxides of manganese. The **carbonate** is precipitated as a white powder from soluble salts by alkaline carbonates. When heated out of contact with air, it gives MnO.

Manganous or Manganese Sulphate, $MnSO_4$, forms several hydrates according to the temperature at which it is crystallized, the most usual one being $MnSO_4, 5 H_2O$. Both this salt and the **chloride** are of a pale pink color. A flesh-colored hydrated **sulphide** is precipitated from their solutions by alkaline sulphides.

The Manganates and Permanganates. — When any compound of manganese is fused with a mixture of potash and saltpeter, a dark green mass is obtained. After extraction with a little water, the solution deposits, on evaporation, crystals of a green salt, **potassium manganate**, K_2MnO_4, which is isomorphous with potassium chromate obtained in a similar way from chromium compounds. **Manganic acid**, H_2MnO_4, which corresponds to this salt, is too unstable to exist, and its anhydride, MnO_3, is very readily decomposed. The manganates are stable in solution only in the presence of much free

alkali.   If the solution is made acid, even with carbonic acid, or if it is largely diluted, the green color changes through many tints to a purple, and a black precipitate is formed at the same time.   On evaporating the purple solution, dark red crystals are obtained of **potassium permanganate**, $KMnO_4$.   The change from manganate to permanganate is shown by the following equations :

$$3\,K_2MnO_4 + 2\,H_2O = 2\,KMnO_4 + 4\,KOH + MnO_2.$$
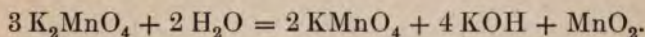
This may be analyzed as follows :

$$3\,K_2MnO_4 + 6\,H_2O = 6\,KOH + 3\,H_2MnO_4;$$
$$3\,H_2MnO_4 = 2\,H_2O + MnO_2 + 2\,HMnO_4;$$
$$2\,HMnO_4 + 2\,KOH = 2\,KMnO_4 + 2\,H_2O.$$
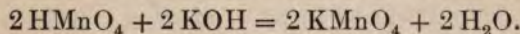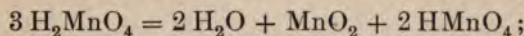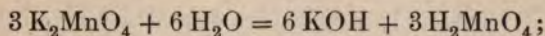
The change from the manganate to permanganate is an oxidation, the valence of manganese being raised from six to seven.   The constitutional formulas, $(KO)_2MnO_2$ and $(KO)MnO_3$, show these valences.

Manganates are not only readily oxidized to permanganates, but are also reduced in either alkaline or acid solutions by oxidizable substances.   In alkaline solutions MnO_2 or lower oxides of manganese are usually precipitated; in acid solutions manganous salts are formed. The equations show the oxygen available for oxidizing :

$$K_2MnO_4 + H_2O = 2\,KOH + MnO_2 + O;$$
$$K_2MnO_4 + 2\,H_2SO_4 = K_2SO_4 + MnSO_4 + 2\,H_2O + 2\,O.$$
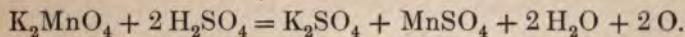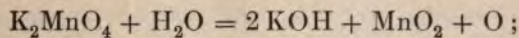
Potassium Permanganate, $KMnO_4$, is made commercially from manganese dioxide by heating this with potassium hydroxide or carbonate with free access of air or with saltpeter to supply oxygen.   The manganate

thus produced is brought into solution and changed into permanganate by means of carbon dioxide or an acid:

$$2 \, MnO_2 + 4 \, KOH + O_2 = 2 \, K_2MnO_4 + 2 \, H_2O.$$
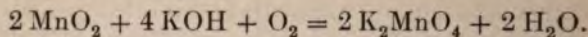
The reaction for the change into the permanganate has already been given. Potassium permanganate crystallizes well, and is easily purified by recrystallization, while the sodium salt, which is made in the same way, is too soluble to crystallize well. The solid salt decomposes readily when heated:

$$2 \, KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$
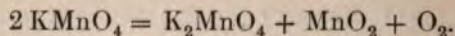
It is a stronger oxidizing agent than potassium dichromate. In powdered form it kindles glycerine when moistened with it. In solution it is used to effect many oxidations. **In alkaline solution** in the presence of oxidizable substances, it is first converted into the manganate:

$$2 \, KMnO_4 + 2 \, KOH = 2 \, K_2MnO_4 + H_2O + O ;$$
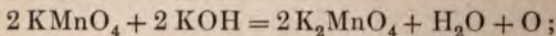
and then the oxidation and accompanying reduction of the manganate proceed as has been already shown. Two molecules of the permanganate supply three atoms of oxygen for oxidation. The complete reaction is:

$$2 \, KMnO_4 + H_2O = 2 \, MnO_2 + 2 \, KOH + 3 \, O.$$
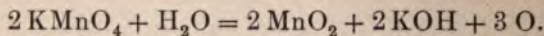
In acid solution all of the manganese is converted into manganous salt, and the amount of available oxygen is greater:

$$2 \, KMnO_4 + 3 \, H_2SO_4 = K_2SO_4 + 2 \, MnSO_4 + 3 \, H_2O + 5 \, O.$$
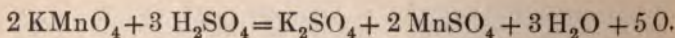
Since the solutions of manganous salts are almost colorless, while the purple color of the permanganate is in-

tense, the slightest excess of permanganate beyond the amount necessary to effect a given oxidation colors the solution. Solutions of permanganate of known oxidizing strength are therefore often used to determine the amount of an oxidizable substance, such as a ferrous salt.

Solid permanganate oxidizes hydrochloric acid with the evolution of chlorine, and when gently warmed with diluted sulphuric acid, oxygen is set free. These reactions furnish convenient methods for making these gases for experimental purposes. The oxidizing power of permanganate solutions makes them good disinfectants. For this use a solution of the cheaper and less pure sodium salt is sold under the name of "Condy's fluid." **Permanganic acid,** $HMnO_4$, and its anhydride, Mn_2O_7, are both very unstable substances.

Detection of Manganese. — Manganese is easily detected by the amethyst color which is imparted to a borax bead by any of its compounds, and by the formation of the manganate when its solid compounds are fused with sodium carbonate and saltpeter. A distinctive precipitate from manganous solutions is the flesh-colored sulphide.

Quantitative Experiments. — Conversion of manganese dioxide, monoxide, carbonate, or sulphate to the red oxide; of the dioxide, red oxide, or carbonate to the monoxide. Determination of the water of crystallization in the sulphate. (See *Quantitative Experiments.*)

CHAPTER XXVIII

IRON

WITH the exception of aluminium, iron is the most abundant of the metallic elements. It is universally distributed. All rocks contain its compounds, and it is found in all soils as the result of the weathering of the rocks. It is one of the dozen elements contained in living matter, and is the heaviest of these. Compounds of iron are necessary to both plant and animal life, and occur particularly in the chlorophyll of plants and in the blood of animals. Free iron occurs in small particles in some basalts and lavas. The most important iron minerals are various oxides, the carbonate, and the sulphides. Red hematite, Fe_2O_3, magnetic iron oxide, Fe_3O_4, brown hematite, $Fe(OH)_3$, and spathic iron, $FeCO_3$, are the chief ores. The sulphide, pyrites, after roasting for the preparation of sulphur dioxide for making sulphuric acid, is now used as a source of iron.

Extraction. — Iron is reduced from its ores by the action of carbon at a high temperature. The process is carried out in **blast furnaces**, which are hollow towers of masonry, often 80 to 100 feet high and about 20 feet in diameter at the widest part, lined with fire brick. Somewhat above the bottom of the furnace tubes enter it, through which hot air is forced, and lower down are openings through which the iron and the slag flow

out. The top of the furnace is closed by a suspended iron cone which is lowered for the introduction of the charge. The gases from the furnace, which contain much carbon monoxide, pass out through a pipe just below the cone and are used for heating the air blast, which enters the furnace at a temperature of about 800°. After the furnace has been heated by a preliminary fire, charges of calcined ore, coke, and flux are introduced from the top, until the furnace is full. A moderate blast is then turned on and very gradually increased for several weeks, until the furnace is in full operation. Meantime and during the working of the furnace, which is continuous, molten iron is drawn off at regular intervals, usually of four or six hours, and the liquid slag flows out of a higher opening, while fresh charges of ore, etc., are added. The life of a blast furnace is often many years. The character of the flux used varies with the nature of the ore. If this is siliceous, limestone is employed ; if the ore contains limestone, sand is used as the flux. The object is to form a fusible slag with the impurities of the ore, thus removing them, and at the same time protecting the reduced iron from oxidation by the blast. Instead of coke, charcoal or anthracite may be used as fuels and reducing agents. The carbon dioxide formed where the blast meets the burning fuel is reduced to carbon monoxide as it passes the higher layers. The ore is partly reduced near the top of the furnace by the carbon monoxide, and as the charge drops to the wider and hotter parts of the furnace, the reduction is completed by the solid carbon, and the iron, combining with carbon to form fusible cast iron, melts and sinks

through the lighter molten slag to the hearth of the furnace.

Cast Iron. — The molten metal drawn from the furnace is guided into channels formed in sand or is run into iron molds, where it forms the rough bars of cast iron known as pig iron ; or is used while still melted for steel making. Cast iron is far from being pure iron. It contains not only carbon, but also silicon, phosphorus, sulphur, and manganese from the impurities of the ore and the flux. Melted iron has the power of dissolving notable amounts of carbon and when the metal cools, part or all of this may be retained in chemical combination with the iron, while any remainder separates out in the metal as graphite. The amount of carbon and its state depend largely on the other substances which are present and the way in which the metal is cooled. Slow cooling favors the crystallization of graphite, while on rapid cooling most of the carbon remains in chemical combination as carbide of iron. The properties of the two products are quite different. When most of the carbon is in the form of graphite, the iron is known as **gray iron**. This melts to a thin liquid and is well adapted for castings because of this fact, and because it expands as it becomes solid. It is also soft enough to be worked in the machine shop, — planed, bored, filed, etc. When the carbon is chiefly present as carbide, the iron is known as **white iron**. This is very hard and brittle, and though it melts at a lower temperature than the gray iron, is less liquid. It is not adapted to castings and is used for making wrought iron and steel. **Mottled** iron is between gray and white iron *in its* composition and properties. When cast iron is

made from ores containing much manganese (5 to 20 per cent), it is called **spiegel iron**. This is used in steel making. All varieties of cast iron contain from 2.5 to 4.5 per cent of carbon and silicon, smaller quantities of phosphorus and sulphur, and usually manganese and other metallic elements. Slight variations in the amounts of these substances have a great effect on the properties of the metal. Cast iron is brittle, so that it cannot be worked under the hammer, and it cannot be welded. By prolonged heating in pulverized iron ore (oxide), castings lose part of their carbon and become somewhat malleable.

When cast iron is dissolved in acids, the graphite present separates in black scales, while the combined carbon unites with hydrogen to form hydrocarbons which impart a disagreeable odor to the gas which is evolved.

Wrought Iron. — This is the purest form of commercial iron. It is made from cast iron by removing the carbon and other substances by oxidation. Most of the wrought iron is made from cast iron by the **puddling process**. The cast iron is melted on a layer of iron oxide (iron ore) in a reverberatory furnace. The impurities are oxidized at the expense of the iron oxide, the carbon going off chiefly as carbon monoxide, while the silicon and phosphorus, after oxidation, combine with the iron oxide to form a slag which also contains the sulphur as iron sulphide. The process is assisted by stirring ("puddling") with iron rods, and as it proceeds, the iron becomes pasty, and is finally withdrawn in a ball ("bloom") which is then brought under a steam hammer to squeeze out the slag and

weld it into a homogeneous mass.   The purest wrought iron still contains from 0.1 to 0.25 per cent of carbon. It is fibrous and tough, softens enough to be welded below 1000°, but melts only at a much higher temperature.   If it contains more than a trace of phosphorus, it is brittle when cold (" cold short "), and a little sulphur makes it brittle when hot ("hot short"), and unsuitable for welding, which is its most valuable property.   Wrought iron is also made to a small extent in bloomery forges, where the iron is reduced from the ore and the impurities are removed in one operation.

As the wrought iron made in the way which has been described is not melted in the process, it is impossible to get rid of traces of slag, and the product is not perfectly homogeneous.   By the Bessemer and open hearth processes, the temperature necessary for complete fusion is reached so that the slag separates by gravity.

The product of the following processes, whether of the same composition as wrought iron, or containing more carbon by addition to the wrought iron first obtained, is known commercially as **steel**.

Bessemer Process. — In this process 10 to 20 tons of cast iron can be converted into wrought iron or steel in 20 to 30 minutes.   Molten white iron from the blast furnace is poured into a large egg-shaped " converter," made of iron and lined with refractory materials.   It is then subjected to an air blast through perforations in the bottom of the converter.   The heat is maintained and increased by the oxidation of the impurities to a *point* above that of the fusion of wrought iron.   The

lining of the converter plays a part in the removal of
the impurities. If the iron is free from phosphorus,
a siliceous lining is used which aids the formation of
slag; if much phosphorus is present, calcium and
magnesium oxides are employed for the lining, and
form phosphates of calcium and magnesium with the
oxidized phosphorus. This last is called the **basic pro-
cess**, and the slag, being rich in phosphates, is ground
up and sold as fertilizer. Any oxide of iron which is
present at the end of the operation may be destroyed
by the addition of a little aluminium.

Open Hearth Process. — This is carried out in a rever-
beratory furnace and is essentially the same as the
puddling process, except that a temperature sufficient
to melt wrought iron completely is obtained by using
fuel gas and air heated by the waste heat of the furnace.
Oxide of iron (ore) is added which oxidizes the impuri-
ties. Silicate or dolomite linings are employed as in
the Bessemer process, and, when phosphorus is present,
lime and limestone are added to the charge. This
process requires much more time than the Bessemer
process, but it gives a better quality of steel.

Steel. — Steel is a name given to many varieties of
iron containing carbon up to 1.5 per cent, with or with-
out the addition of other metals. It is mostly made
by the Bessemer or open hearth process by adding to
the wrought iron, which is the immediate product,
spiegel iron, or other alloys of iron in such amounts as
to give to the steel the desired composition. Steel is
also made in small quantities by other methods. In
the **cementation process**, wrought iron bars are packed
in powdered charcoal or soot, and heated to a red heat

for several days. **Crucible steel** is made by melting bars of cemented steel in a graphite crucible, either alone or with iron of various qualities and with carbonizing or decarbonizing materials. It is employed for the best grades of cutlery.

Steel which contains the least amount of carbon (about 0.2 per cent) is called mild steel and is much the same as wrought iron. By varying the proportion of carbon and by the addition of other metals, such as manganese, chromium, nickel, etc., the properties of steel may be widely varied and the metal adapted to many different uses.

The most characteristic property of steel is that of becoming exceedingly hard and brittle when suddenly chilled from a high temperature. When slowly cooled it is soft, and the hardness produced by rapid cooling may be modified to any extent by reheating the hardened steel to definite temperatures. This is called "tempering." The temperature to which the steel is heated for tempering is judged by the interference colors in the film of oxide which is produced. The temperature for tempering different articles varies from 230° (pale yellow) for razors, etc., to about 300° (dark blue) for saws, etc. The tempered steel is elastic. The changes produced in steel and in cast iron by slow or sudden cooling are explained by the existence of different allotropic states of iron, and the different admixtures or alloys of these states and of the carbide of iron and graphite which are present. The result is also modified by the presence of other metals, which contribute properties of their own to the product. Hardened steel is a solid solution of the carbide, Fe_3C,

in the modification of iron which is stable at a high temperature, and which in the rapid cooling has not had time and opportunity to change into the other modification which is stable at lower temperatures. On slow cooling, this change occurs, the carbide separates, and also graphite, if sufficient carbon is present.

Properties. — The purest form of commercial iron is the wrought iron used for piano wire, and this contains about 0.15 per cent of impurity. Pure iron may be obtained as a black powder by heating the pure oxide or oxalate in hydrogen. If the reduction is carried on at the lowest possible temperature, the iron is "pyrophoric" and becomes red hot from oxidation when exposed to the air ; but when reduced at a high temperature, this does not occur. Pure iron may also be prepared by the reduction of its chloride in hydrogen and by the electrolysis of ferrous solutions. Pure iron softens at a red heat, but melts less readily than wrought iron. Like all varieties of iron, it is attracted by the magnet and becomes magnetic, but does not retain this property ; while steel can become permanently magnetized. Iron burns in oxygen and decomposes water at a red heat with the formation of Fe_3O_4. It also combines with the halogens directly, and forms the sulphide, FeS, when heated with sulphur. Dilute hydrochloric and sulphuric acids dissolve iron with evolution of hydrogen and formation of ferrous salts. Dilute nitric acid, when cold, produces ferrous and ammonium nitrates. In concentrated nitric acid, iron becomes " passive," being superficially changed so that the dilute acid does not act on it. Iron rusts in moist air, and as the rust is too spongy to protect the metal, as in the case of zinc

and copper, the action may go on until the metal is completely converted into rust. **The rusting of iron** is not a simple oxidation, and though the rust is largely ferric hydroxide, the carbon dioxide of the air appears to play an important part in the process. The rusting begins slowly, but when a layer of rust has once formed, it goes on rapidly. Alkalies prevent it, and it is promoted by certain salts, especially by those of ammonium. Iron is often protected from rusting by a coating of tin or zinc. The sheet iron or wire is first cleaned and then dipped in the molten metal. Ordinary "tin" is wrought iron or steel coated in this way with an adherent film of tin. As iron is more electropositive than tin, the protection not only fails when the tin is removed at any point, but the rusting goes on more rapidly than if the iron were not in contact with tin. Zinc, on the other hand, is more electropositive than iron, and gives a certain amount of protection even when the film is broken. Paints, oils, and graphite are also used to protect iron from rust; and a film of oxide, produced by heating iron in superheated steam, as in the Barff process, is an excellent protection.

Iron acts both as a divalent and as a trivalent element, forming two series of compounds which are distinguished as ferrous and ferric. Solutions of ferrous salts are usually green; those of ferric salts, yellow.

Oxides of Iron. — **Ferrous oxide,** FeO, may be prepared as a black powder by heating ferrous oxalate, or by careful reduction of the other oxides by hydrogen. **Ferric oxide,** Fe_2O_3, may be prepared by ignition of the precipitated ferric hydroxide, and is a by-product in *some* industries. It is sold as "rouge" and "Venetian

red " and used as a pigment and as a polishing powder. When it has been strongly heated, it is nearly insoluble in acids. Though a basic oxide, it combines with some other metallic oxides to form compounds which may be regarded as **ferrites** of the composition of $Zn(FeO_2)_2$. This occurs naturally as franklinite. **Ferro-ferric oxide,** Fe_3O_4, which occurs as magnetite, may be assumed to be ferrous ferrite, $Fe(FeO_2)_2$. This oxide is formed when iron is heated to redness in the air as a black scale, and when iron is heated in steam or in carbon dioxide. All of the oxides of iron are readily reduced to the metal when heated in hydrogen.

FERROUS COMPOUNDS

Ferrous Sulphate, $FeSO_4$. — When iron is dissolved in sulphuric acid a green solution is obtained which yields green crystals of ferrous sulphate, $FeSO_4, 7H_2O$. This salt, which is commonly known as "green vitriol," is isomorphous with the sulphates of zinc, magnesium, and copper. It is produced by the natural oxidation of pyrites and is obtained in large quantities from the weathering of this mineral. The heaps of pyrites are sprayed with water, and the solution runs into tanks where it is treated with scrap iron to convert the acid, which has been formed, into ferrous sulphate, and to reduce the ferric sulphate which is always present. The solution is then evaporated to crystallization. The salt is also a by-product of several industries in which sulphuric acid is employed, as in foundries and wire mills, and in petroleum refining. The crystals effloresce on exposure to the air and become brownish from oxida-

tion to basic ferric sulphate. On heating in air, oxidation occurs before all of the water of hydration is given off, and ferric oxide is left. Anhydrous ferrous sulphate can be obtained by heating the salt with exclusion of air. It is a white, very hygroscopic powder. In solution, ferrous sulphate is slowly oxidized by oxygen absorbed from the air. A double salt, ferrous ammonium sulphate, $(NH_4)_2SO_4, FeSO_4, 6 H_2O$, is much more stable, and is often used in the laboratory when a solution of a ferrous salt is desired. Ferrous sulphate is the most important of the iron salts. It is largely used under the name of green vitriol and copperas in dyeing, in making inks and prussian blue, as a disinfectant, and as a reducing agent for precipitating gold from solutions obtained from the ores. Ferrous sulphate reduces nitric acid to nitric oxide, which forms an unstable dark compound with an excess of the sulphate. This reaction is employed as a test for nitric acid.

Some Other Ferrous Compounds. — **Ferrous Chloride**, $FeCl_2, 4 H_2O$, is obtained from the solution formed by the action of hydrochloric acid on iron, and the anhydrous salt, $FeCl_2$, appears as a colorless crystalline sublimate when hydrogen chloride is led over heated iron.

Ferrous Hydroxide, $Fe(OH)_2$, is formed as a white precipitate on the addition of alkalies to ferrous solutions which are free from ferric compounds. It rapidly becomes greenish and finally brown by oxidation in the air.

Ferrous Sulphide, FeS, is made by heating iron and sulphur together, or by heating pyrites in a current of hydrogen. It is not reduced by hydrogen. It is commonly employed as the source of hydrogen sulphide

for laboratory purposes. As the commercial sulphide always contains free iron, the hydrogen sulphide obtained from it by the action of the acids is mixed with hydrogen. Ferrous sulphide is also precipitated from ferrous solutions by ammonium sulphide. The moist sulphide slowly oxidizes in the air to ferrous sulphate.

FERRIC COMPOUNDS

Ferric compounds are readily obtained by oxidation of ferrous compounds. Ferrous sulphate in solution is converted into a mixture of **ferric sulphate**, $Fe_2(SO_4)_3$, and nitrate by nitric acid:

$$3\,FeSO_4 + 4\,HNO_3 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + 2\,H_2O + NO.$$
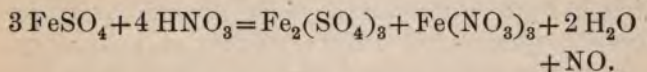
If sufficient sulphuric acid then is added, the brown solution gives on evaporation a sirupy liquid, from which the white anhydrous sulphate can be obtained by heating. Too high a temperature decomposes it into sulphur trioxide and ferric oxide. It is an alum forming sulphate.

Ferric Chloride, $FeCl_3$, may be made by leading chlorine into a solution of ferrous chloride. It forms a yellow solution from which deliquescent crystals of the hydrated salt may be obtained. **Ferric hydroxide** precipitated by alkalies from ferric solutions easily becomes colloidal in a solution of ferric chloride and can be obtained in pure solution by dialysis. (*Cf.* p. 201.)

Ferric Sulphide, Fe_2S_3, corresponding to ferric oxide, is of little importance, but a persulphide, FeS_2, is the abundant and well-known pyrites. It gives off part

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of its sulphur when heated, oxidizes in the presence of air and water to ferrous sulphate (p. 335), and the sulphur dioxide produced by burning it is largely used in making sulphuric acid. It is not attacked by dilute acids, and is reduced to ferrous sulphide by hydrogen. Since pyrites gives ferrous sulphate on oxidation, the iron in it appears to be in the ferrous condition, so that

the formula would be $Fe{<}^{S}_{S}$.

Some very unstable **ferrates**, such as K_2FeO_4, can be made, corresponding to the chromates. They are of interest only in tracing an analogy between the compounds of iron, chromium, and manganese. In them iron appears as a hexavalent element.

Reduction and Oxidation of Iron Compounds. — Ferric compounds are readily reduced to ferrous compounds by various reducing agents, and we have seen that oxidation of ferrous to ferric compounds is often spontaneous. An excellent method for determining iron depends upon the oxidation of ferrous to ferric iron by potassium permanganate. The iron is brought into the ferrous state in solution by reduction, if necessary, with sulphuric acid and zinc. The solution is then oxidized by a permanganate solution whose oxidizing power for each cubic centimeter is known. During the oxidation the permanganate loses its color, but when the iron is all oxidized, the slightest excess of permanganate colors the solution pink. From the amount of permanganate solution used, the amount of iron is easily calculated. The facility with which ferric compounds are reduced and ferrous compounds are oxidized explains the rotting

of cloth stained with iron rust. The rust acts as contact agent, parting with oxygen to the fibers with simultaneous reduction to the ferrous condition. The ferrous oxide is then reoxidized by the air. The loosening of iron nails in exposed woodwork is due to a similar reaction.

Ferro- and Ferricyanides. — Besides the comparatively simple ferrous and ferric compounds which have been described, there is a group of important substances of more complex character which contain iron and the cyanogen group (p. 183). When potassium cyanide is digested with a solution of a ferrous salt, there may be obtained, by subsequent evaporation, lemon-yellow crystals which have the composition $K_4Fe(CN)_6$. This is **potassium ferrocyanide**, or "yellow prussiate of potash." It is made by heating a mixture of crude potash, iron filings, and organic matter, such as clippings of horn or leather, or dried blood, and treating the mass, after cooling, with water. The crude salt is deposited on evaporation of the solution and purified by recrystallization. It is also obtained as a by-product in making coal gas, and in other industries.

The crystals are unaltered in air and are converted into the white anhydrous salt at 110°. Heated more strongly, the salt is decomposed with the formation of potassium cyanide (p. 273). The solution of potassium ferrocyanide, when exposed to the air, is slowly oxidized with the separation of prussian blue. This tendency to oxidation indicates that the iron is in the ferrous or divalent condition. On leading chlorine into the solution and evaporating, dark red crystals are obtained of the **ferricyanide**, $K_3Fe(CN)_6$, or "red prussiate of pot-

ash," the iron having been oxidized to the trivalent ferric condition:

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,KCl + 2\,K_3Fe(CN)_6.$$
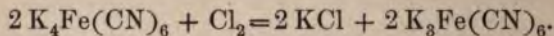
This is another illustration of an oxidation in the larger meaning of the term, oxygen playing no part in the reaction, but the valence being raised.

Neither of these salts gives the usual tests for iron, such as precipitation by alkalies, since the iron is present in the group or ion $Fe(CN)_6$. This group is an acid group, and the ferrocyanic and ferricyanic acids which correspond to the two salts can be obtained. In the ferro-salt and acid the group is quadrivalent, and in the ferri-salt and acid it is trivalent, as the formulas show. The six cyanogen groups have six valences and two are satisfied by ferrous iron in the ferro-compounds and three by ferric iron in the ferri-compounds.

Potassium ferricyanide is an oxidizing agent like most of the ferric compounds. It is reduced by hydrogen peroxide with disengagement of oxygen:

$$4\,K_3Fe(CN)_6 + 2\,H_2O_2 =$$
$$3\,K_4Fe(CN)_6 + H_4Fe(CN)_6 + 2\,O_2.$$
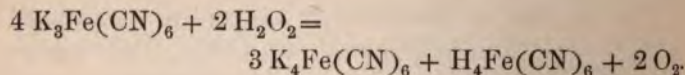
Potassium ferro- and ferricyanides react with solutions of the salts of many metals, giving ferro- and ferricyanides of these metals. Of especial interest to the chemist are the reactions with iron salts, as these serve not only for the detection of iron, but also to show whether it is present in the ferrous or ferric condition. *With* ferric salts, potassium ferrocyanide gives a blue

precipitate of "prussian blue," with ferrous salts, a white precipitate; while potassium ferricyanide gives a blue precipitate of "Turnbull's blue" with ferrous salts, and a brown color but no precipitate with ferric salts. Both blue precipitates are complex salts whose constitution is not thoroughly known. Prussian blue can be obtained in a state soluble in water by adding a ferric solution slowly to an excess of ferrocyanide, or by boiling prussian blue in a ferrocyanide solution. It is used for "bluing." Commercial prussian blue for dyeing and calico printing is usually made by oxidizing the white precipitate formed by potassium ferrocyanide and the cheap iron vitriol, by means of nitric acid or bleaching powder.

Photographic Blue Printing depends on the reduction of ferric salts by light. The paper is prepared by wetting it with a mixed solution of potassium ferricyanide and a ferric salt (usually the citrate) and then drying it in the dark. When exposed to light, reduction occurs; and when brought into water Turnbull's blue is produced where the light has acted, while the unchanged salts are washed away from the protected portion, leaving the white paper. The water is thus at once a developing and fixing agent, and the print after thorough washing is permanent.

Detection of Iron. — Iron is detected in its solid compounds by the bottle-green color imparted to the borax bead in the reducing flame of the blowpipe, which changes to a pale yellow in the oxidizing flame. In solutions iron is readily recognized by the various precipitations with reagents, and ferrous and ferric iron are distinguished by the reactions with potassium ferro- and

ferricyanides, and ferric salts by the blood-red color produced by potassium thiocyanate.

Quantitative Experiments. — Determination of the hydrogen equivalent; conversion of iron into oxide, sulphide, or sulphate; of the oxide into iron; and of the disulphide (pyrites) into sulphide. (See *Quantitative Experiments.*)

CHAPTER XXIX

NICKEL AND COBALT

COBALT and nickel usually occur together in combination with sulphur and arsenic, and the ores commonly contain other metals. The treatment of the ore varies according to its nature and is usually rather complicated. The object is to obtain the metals in the form of oxides, which can then be reduced to the metals.

Cobalt has no practical uses, and is not prepared commercially. It may be obtained by the reduction of the oxide or chloride when heated in hydrogen, as a gray powder, or in a compact form by the thermite process. It may also be deposited from its solution by electrolysis.

Nickel is reduced from its oxide by carbon. In practice, the oxide is pressed into small cubes and these are strongly heated in charcoal powder. The reduced metal retains the cubical form. An interesting process proposed for extracting nickel depends on the formation and decomposition of a peculiar compound, nickel carbonyl, $Ni(CO)_4$, which finely divided reduced nickel forms with carbon monoxide at 80°. This compound, which is a liquid at ordinary temperature, boils at 43°, and the vapor decomposes into nickel and carbon monoxide when passed through tubes heated to 200°.

Nickel is used for making dishes and crucibles for

many laboratory purposes; but its large use is for electro-plating iron and other metals, and in making alloys. The more important of these alloys are: german silver, containing copper, nickel, and zinc; nickel coins, copper and nickel; and nickel steel.

The atomic weights of the two metals are nearly the same, and they are very similar in their properties. Both resemble polished iron in appearance, and like iron are malleable and tough. They are somewhat harder and heavier than iron, and are magnetic, though much less so than iron, and oxidize less readily. Both dissolve readily in dilute nitric acid and are rendered "passive," like iron, by the concentrated acid. Hydrochloric acid and dilute sulphuric acid dissolve both metals, but act on nickel less readily than on cobalt. The salts of both metals form many complex compounds with ammonia.

COMPOUNDS OF COBALT AND NICKEL

Cobalt and nickel form oxides and hydroxides similar to those of iron, in which they act as divalent and as trivalent elements. Cobalt forms both cobaltic and cobaltous salts, though the former are not very stable, while no nickelic salts are known.

Oxides. — Three well-defined oxides of cobalt are known; CoO, Co_3O_4, and Co_2O_3. The black **cobalto-cobaltic oxide**, Co_3O_4, is always formed when the other oxides or the nitrate are strongly heated in air. When the nitrate is decomposed at the lowest possible temperature, **cobaltic oxide**, Co_2O_3, is produced. **Cobaltous oxide**, CoO, may be obtained by cautious reduction at a *low* temperature of the other oxides in hydrogen; at

a higher temperature all of the oxides are reduced by hydrogen to metal. An unstable red **cobaltous hydroxide**, $Co(OH)_2$, is made by adding sodium hydroxide to a cobaltous solution and boiling; **black cobaltic hydroxide**, $Co(OH)_3$, is precipitated by hypochlorites.

Nickelic oxide, Ni_2O_3, is obtained by careful heating of the nitrate. It is a black powder which changes into green **nickelous oxide**, NiO, on further heating. Both oxides are easily reduced when heated in hydrogen. Green **nickelous hydroxide**, $Ni(OH)_2$, and black **nickelic hydroxide**, $Ni(OH)_3$, are precipitated in the same way as the cobalt compounds, but the nickelic hydroxide is much less easily precipitated than the cobaltic hydroxide.

Sulphides of both metals are precipitated from their solutions by ammonium sulphide and, when once formed, are insoluble in dilute hydrochloric acid.

Salts. — The hydrated salts of cobalt and their solution are mostly red or pink in color, while nickel salts are green. In the anhydrous state, cobalt salts are blue, and those of nickel, yellow. The change in the color of the cobalt salts is used in the so-called "sympathetic ink." If a dilute solution of cobalt chloride is used as a writing fluid, the dried writing is almost or quite invisible, but when the water of hydration is driven off by heating, the lines appear in blue, disappearing again in moist air. This color change has also been employed to indicate the humidity of the air in toy hygroscopes.

A **double sulphate of nickel and ammonium**, $(NH_4)_2SO_4$, $NiSO_4,6 H_2O$, isomorphous with ferrous ammonium sulphate, is used in the solution for nickel plating.

Cyanides. — The cyanides, $Co(CN)_2$ and $Ni(CN)_2$, are precipitated from cobalt and nickel solutions by potassium cyanide, and are dissolved in an excess of this reagent with the formation of double salts. Acids precipitate the cyanides again; but if the solutions are treated with an oxidizing agent, such as chlorine, the nickel cyanide alone is precipitated by an acid, or by a hypochlorite, the cobalt remaining in solution. This gives a means for separating cobalt and nickel. The double cyanide of potassium and cobalt first formed is potassium cobaltocyanide, $K_4Co(CN)_6$, which corresponds to the ferrocyanide; on oxidation it is converted into the cobalticyanide, $K_3Co(CN)_6$, analogous to the ferricyanide. Nickel does not appear to form similar salts. When a solution of potassium nitrite is added to a solution of a cobalt salt made acid with acetic acid, the cobalt is oxidized and a complex compound of cobalt, $K_3Co(NO_2)_6, nH_2O$, known as Fischer's salt, is precipitated. As solutions of nickel are not precipitated by this treatment, the two metals can be separated by this reaction.

Smalt is a powdered silicate or glass of potassium and cobalt made by fusing the crude cobalt oxide obtained from the ore with sand and potash. It is used as a pigment for painting on porcelain, but does not work well in oil or water colors. It is now largely superseded by ultramarine (p. 311). Another blue cobalt pigment is obtained by heating together cobalt phosphate and aluminium hydroxide. This "cobalt blue" makes a good oil color. A similar color is produced when any compound of aluminum is heated with cobalt nitrate, and this is used in the laboratory as a

test for aluminium. Cobalt nitrate and zinc compounds, when ignited together, yield a ·green mass which is employed for the detection of zinc in its compounds.

Detection of Cobalt and Nickel. — The presence of cobalt in its compounds is readily detected by the intense blue color which it imparts to the borax bead. Nickel compounds produce a rather slight brownish yellow in the oxidizing flame of the blowpipe, and the bead becomes gray and opaque in the reducing flame. In solution, both metals are recognized by the colors of their salts and by reactions which have been described.

Quantitative Experiments. — Conversion of cobalt into oxide or sulphate; reduction of oxide to cobalt by hydrogen. Conversion of nickel into oxide, sulphide, or sulphate; of the oxide into nickel or sulphate. (See *Quantitative Experiments.*)

CHAPTER XXX

TIN AND LEAD

BOTH tin and lead have been known and used since the earliest times of which we have records. The metals were not, however, clearly distinguished from each other; Pliny calls them plumbum candidum and plumbum nigrum respectively, and they were apparently considered varieties of one metal rather than distinct metals.

Tin and lead are the softest of the useful metals and among the most fusible. Both are readily reduced from their oxides when these are heated with carbon or hydrogen.

TIN

Properties. — Tin is a white, lustrous metal whose specific gravity is somewhat less than that of iron, and which melts at a lower temperature than any useful metal except mercury. It is slightly harder than lead, but softer than zinc. It is malleable and can be rolled or beaten into thin foil. At 100° it can be drawn into wire, which, however, has little strength. At 200° it becomes so brittle that it may be powdered in a mortar. Melted tin solidifies in a mass of interlacing crystals, and when a bar of tin is bent, a crackling is heard due to the friction of the crystals on each other. If the bar *is* bent back and forth quickly, it becomes warm. The

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crystalline texture of tin is revealed when the film of tin on ordinary tin plate is etched with a dilute solution of aqua regia.

Under the influence of low temperatures massive tin sometimes crumbles into a gray powder. This is an allotropic form of tin which is much lighter than ordinary tin, and which is the stable variety of tin below 20°. Ordinary tin below this temperature is therefore in a metastable condition; but the change to gray tin usually takes place very slowly or not at all, unless some gray tin is in contact with it. The most favorable temperature for the change is −48°. This disintegration of compact tin has been observed many times, in Russia and Finland, in tin bars, roofing, and organ pipes.

Tin does not tarnish in air at ordinary temperatures, but is slowly oxidized when melted, and at a high temperature burns to the dioxide. It combines directly with the halogens, and hydrochloric acid dissolves it with the evolution of hydrogen. Hot, concentrated sulphuric acid acts on it with the formation of stannous sulphate and sulphur dioxide:

$$Sn + 2\,H_2SO_4 = SnSO_4 + 2\,H_2O + SO_2.$$
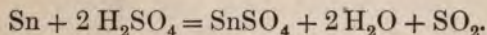
Dilute nitric acid at 0° dissolves tin with the production of stannous nitrate, but the usual action of nitric acid results in the formation of a white insoluble powder which is called metastannic acid. Tin is also acted on by strong solutions of the caustic alkalies with the evolution of hydrogen and the formation of soluble metastannates.

Uses of Tin. — Tin is used to some extent in making "block tin" pipes and stills, and tin foil; but its largest

employment is in tinning iron and in making alloys.
Common pins are made of brass wire and coated with
tin by means of a solution of a tin salt from which tin
is displaced by some of the zinc of the brass.   Sheet
copper is frequently tinned on one side, to prevent its
corrosion, by rubbing melted tin on the cleaned surface
with tow.   Common solder and pewter are alloys of
tin and lead; britannia metal is tin with antimony and
some copper; gun metal, bell metal, speculum metal,
and various bronzes are alloys of tin and copper in differ-
ent proportions.   Tin amalgam was formerly used for
"silvering" mirrors.

Occurrence. — Tin rarely occurs native.   It is found
in small quantities combined with sulphur and other
metals and as silicate, but the principal mineral and
only ore of tin is tinstone, which is a more or less pure
form of the dioxide, SnO_2.   This ore is not very gener-
ally distributed, and most of the world's supply of tin
comes from the Cornwall mines, which have been con-
tinuously worked from the time of the Roman occupa-
tion of England, and from the rich deposits found in
Banca and other islands of the East Indies.

Extraction. — The ore is coarsely pulverized and the
admixed rock separated from the heavier tinstone by
washing.   The latter is roasted to drive off the arsenic
which may be present and to oxidize the sulphides of
copper and iron.   It is then washed a second time to
remove the oxidized material, and is finally mixed with
coal and heated in a reverberatory furnace.   The crude
tin thus obtained is refined by melting it and running
the metal at a temperature just above its melting point
through a filter consisting of sheets of tinned iron

pressed together. The final impurities, being less fusible than the tin, are left on the filter. The purest tin is obtained from the Banca mines. Some tin is recovered from old tin cans and tin plate scrap.

COMPOUNDS OF TIN

Tin is both divalent and tetravalent, and forms two series of compounds, the stannous and stannic. The two chlorides of tin are the most important salts of this metal.

Stannous chloride, $SnCl_2$, is obtained in solution when hydrochloric acid acts on tin. On evaporation it crystallizes as $SnCl_2, 2 H_2O$. This is known commercially as "tin salt." The salt is partly decomposed on heating; and when a strong solution of it is diluted, it is partly hydrolyzed with the precipitation of a basic chloride, $Sn(OH)Cl$. This hydrolysis may be prevented by the addition of hydrochloric acid. The solution of stannous chloride is a strong reducing agent, since it tends to become stannic chloride. It reduces ferric chloride to ferrous chloride:

$$2 FeCl_3 + SnCl_2 = 2 FeCl_2 + SnCl_4;$$
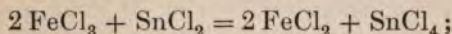
and precipitates the insoluble mercurous chloride, or even mercury, from solutions of mercuric chloride:

$$2 HgCl_2 + SnCl_2 = 2 HgCl + SnCl_4;$$
or $$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$
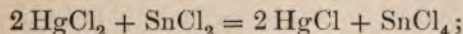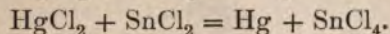
Solutions of stannous chloride are oxidized also by standing in the air, and neutral solutions become turbid from the production of the basic salt:

$$6 SnCl_2 + 2 H_2O + O_2 = 2 SnCl_4 + 4 Sn(OH)Cl.$$
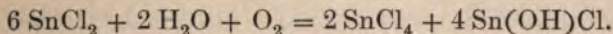
The solution may be rendered clear again by adding some metallic tin and hydrochloric acid.

Stannous chloride is used as a reducing agent in the laboratory and as a mordant in dyeing.

Stannic chloride, $SnCl_4$, may be made by the action of chlorine on tin or on stannous chloride. In the anhydrous state, or when formed by the direct union of chlorine and tin, it is a colorless liquid which boils at 114°, and whose vapor density corresponds very nearly with that required by its formula. It fumes strongly in moist air because of the hydrogen chloride set free by hydrolysis. It forms various hydrates with water, one of which, $SnCl_4,5 H_2O$, known as the "oxymuriate of tin," is used as a mordant. In dilute solutions it is hydrolyzed, and the reaction may become almost complete on standing or on boiling. Stannic chloride readily forms double salts with other chlorides, and one of these, with ammonium chloride, has been much used as a mordant under the name of "pink salt."

The other salts of tin are readily hydrolyzed with the formation of basic salts or hydroxides.

Hydroxides; Stannates. — The hydroxides and carbonates of the alkalies give white precipitates of hydroxides in solutions of both of the chlorides. The precipitated hydroxides act as weak acids and dissolve in an excess of sodium or potassium hydroxide because of the formation of soluble stannites and stannates. **Stannous hydroxide**, $Sn(OH)_2$, is an unstable compound, and the precipitate by sodium carbonate is a partly dehydrated hydroxide, $Sn_2O(OH)_2$. This is readily oxidized in the air, and in absence of air is easily changed into stannous oxide, SnO. It gives stannous salts with acids, and

with alkalies forms stannites which are decomposed by boiling their solutions into stannates and metallic tin:

$$2\,Na_2SnO_2 + H_2O = Na_2SnO_3 + 2\,NaOH + Sn.$$
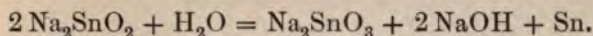
The gelatinous **stannic hydroxide** precipitated from stannic chloride is given the formula $(HO)_2SnO$, but neither this nor the normal hydroxide, $(HO)_4Sn$, is obtained as a definite compound. When heated it is converted into the dioxide, SnO_2. With acids it gives stannic salts, and with alkalies, soluble stannates, such as Na_2SnO_3. Sodium stannate is obtained from its solutions in the hydrated form $Na_2SnO_3,3\,H_2O$, and is used as a mordant under the name of "preparing salt." The hydroxide, H_2SnO_3 or $(HO)_2SnO$, from which the stannates are derived is called **stannic acid**. A similar compound is obtained by the action of nitric acid on tin and is called **metastannic acid**. It differs from stannic acid in being less readily soluble in acids and in alkalies, and in yielding stannates of different composition, such as sodium metastannate, $Na_2Sn_5O_{11}$ (*cf.* silicates, p. 202). On fusion with caustic alkalies, however, metastannic acid gives stannates which are the same as those obtained from stannic acid.

Oxides. — **Stannous oxide**, SnO, is a dark-colored substance which may be obtained by heating stannous hydroxide, or oxalate (SnC_2O_4), out of contact with air. It is readily oxidized to stannic oxide when heated in air. **Stannic oxide**, SnO_2, is formed as the final oxidation product of tin when the metal or stannous oxide is burned in the air, and is also obtained by heating stannic or metastannic acid. It is a white or slightly yellowish powder which becomes distinctly yellow while hot.

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Sulphides. — Dark brown **stannous sulphide**, SnS, and yellow **stannic sulphide**, SnS_2, are precipitated from the solutions of corresponding tin salts by hydrogen sulphide. Stannic sulphide dissolves in alkaline sulphides, and stannous sulphide in alkaline polysulphides, with the formation of sulphostannates, from whose solutions stannic sulphide is precipitated by acids. Stannous sulphide may also be made by heating tin and sulphur together, and is produced when stannic sulphide is strongly heated. Stannic sulphide can also be made in the dry way by heating a mixture of tin, sulphur, and ammonium chloride. The sulphide remains in the form of yellow scales which are used for bronzing under the name of "mosaic gold."

Detection of Tin. — Solid compounds of tin are readily reduced to the metal when heated with sodium carbonate on charcoal before the blowpipe. The metal thus obtained is soluble in hydrochloric acid, and the solution gives a white precipitate with mercuric chloride. From solutions of tin salts, zinc precipitates metallic tin in spongy form; hydrogen sulphide precipitates the sulphides, which are dissolved by yellow ammonium sulphide.

Quantitative Experiments. — Determination of the hydrogen equivalent ; conversion of tin into the oxide; of the oxide into tin ; of stannic sulphide into stannous sulphide.   (See *Quantitative Experiments.*)

LEAD

Properties. — Lead is the heaviest of the metals in common use. It is very soft, unelastic, and so yielding that it can be rolled into thin foil, hammered into any

form, and forced by heavy pressure to flow like a thick
liquid, as in making pipes. Its tensile strength is less
than that of the other useful metals, and it cannot be
drawn into fine wire.

It is a grayish white, lustrous metal, whose fresh
surfaces soon become dull and dark from atmospheric
action, and the closely adherent film produced protects
the metal from further corrosion by the air. It melts
very easily, though at a higher temperature than tin,
and a gray scum of oxide forms on the surface of the
molten lead. At higher temperatures this is changed
to other oxides which vary in color from yellow to red.
Hydrochloric and sulphuric acids act very slowly on
lead, but it is readily converted into the soluble nitrate
by nitric acid.

Pure water, containing oxygen in solution from the
air, acts on lead with the production of the somewhat
soluble hydroxide ; and natural waters which contain
salts of ammonium, and especially the nitrate of ammo-
nium, dissolve lead slowly. The presence of carbonates,
sulphates, and some other salts retards or prevents this
action by forming a protective coating on the lead. As
these salts are found in most domestic waters, lead
pipes may be usually employed without danger of con-
taminating the water with compounds of lead. All of
the soluble compounds of lead are poisonous, and, as
this action is cumulative, the presence of minute amounts
in drinking water is to be avoided. Lead is attacked
and dissolved slightly by acetic acid, and the organic
acids of fruits and vegetables, so that the contact of
lead or its alloys with foods may be dangerous. Lead
is both divalent and tetravalent in its compounds.

Uses. — Lead is used, on account of its small activity towards ordinary chemical agents, in pipes for plumbing and for protecting electric cables, and in sheet form for lining tanks and sulphuric acid chambers. It is also used in making storage batteries and, alloyed with a little arsenic, for shot and bullets. It is a component of a number of important alloys with tin, which have been mentioned, and of some fusible alloys. Type metal is an alloy of lead with antimony.

Occurrence and Extraction. — Lead is very seldom found in the native state, but is widely distributed as sulphide in galena, and also occurs as oxide, chromate, sulphate, as well as in some other compounds. Practically all the lead for the world's supply is obtained from galena. Lead is easily reduced from the sulphide by three different processes. 1. When the ore is comparatively pure, the **air reduction process** is used : the galena is roasted until part is converted into oxide and part into sulphate, and at a higher temperature, these compounds react with the unaltered sulphide, producing sulphur dioxide and lead :

$$2\,PbO + PbS = 3\,Pb + SO_2 ;$$
$$PbSO_4 + PbS = 2\,Pb + 2\,SO_2.$$
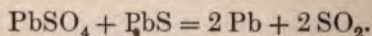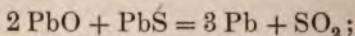
2. The oxide produced by more complete roasting is reduced by carbon with the addition of fluxes, in small blast furnaces, very much as in the reduction of iron from its ores :

$$PbO + C = Pb + CO.$$
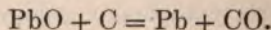
3. The sulphide is heated with iron :

$$PbS + Fe = Pb + FeS.$$
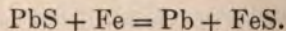
Softening of Lead. — The crude lead from these processes is hard because it contains small amounts of other metals and some sulphides. Silver is always present, and the amount extracted from crude lead forms a considerable part of the annual production. The lead must be purified to render it soft and malleable, and most of the other impurities must be removed before extracting the silver. The lead is melted and kept at a temperature just above its melting point. Under these conditions the copper present separates out in an alloy which is less fusible than the lead, and all the other usual impurities except bismuth are oxidized, forming a dross which is removed.

Desilverization. — The silver contained in lead can be extracted by oxidizing all of the lead by heating in a current of air; but this is not profitable unless the lead contains at least 8 ounces of silver to the ton, and much of the crude lead carries less than this. The **Parkes' process** for removing the silver depends on the fact that while melted lead and zinc dissolve only slightly in each other, zinc and silver mix freely and form an alloy which solidifies while the lead is still melted. After the addition to the melted lead of the small amount of zinc which is necessary, the metal is allowed to cool, and the lighter silver-zinc alloy rises to the surface, where it solidifies and is removed by a perforated ladle. The little zinc remaining in the lead is removed by oxidation. The silver can also be concentrated for profitable extraction by **Pattinson's process**, in which advantage is taken of the fact that when an alloy of lead with a little silver is melted and allowed to cool, pure lead crystallizes out first, leaving an alloy richer in silver.

Commercial lead after these processes of purification is very nearly pure.

Oxides. — Lead forms five oxides. **The suboxide,** Pb_2O, is a gray powder which is formed as the first oxidation product of lead when it is heated in air, and also by gently heating lead oxalate. When lead is further oxidized the **monoxide,** PbO, is produced. This is a by-product in the extraction of silver from lead-silver alloys. When it is formed at a high enough temperature for its fusion, it is a yellowish red substance known as "litharge." The unmelted oxide, such as is obtained by decomposition of the carbonate or nitrate of lead, is called "massicot." By heating massicot carefully, and with frequent stirring, to a dull red heat, it is slowly changed into **red lead** or **minium,** Pb_3O_4. Red lead usually contains some monoxide, and the latter is usually not free from red lead. The **sesquioxide,** Pb_2O_3, is formed by the action of a hypochlorite on a solution of the monoxide in caustic potash. This oxide and the suboxide are of little importance. **Lead dioxide,** PbO_2, can be formed by treating red lead with dilute nitric acid:

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + 2\,H_2O + PbO_2;$$
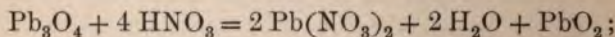
or by oxidation of lead salts by hypochlorites. It is a brown powder which is an active oxidizing agent. It acts on hydrochloric acid with the production of chlorine:

$$PbO_2 + 4\,HCl = PbCl_2 + 2\,H_2O + Cl_2;$$
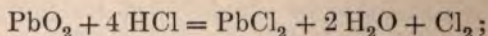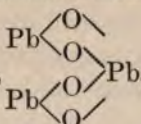
and unites directly with sulphur dioxide to form lead sulphate:

$$PbO_2 + SO_2 = PbSO_4.$$
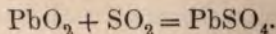
All the other oxides of lead are converted into the monoxide when strongly heated in air, the suboxide being oxidized and the others losing oxygen.
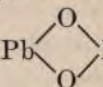
In the monoxide lead is divalent, in the dioxide, tetravalent. In the red lead both divalent and tetravalent lead are considered present, $Pb\underset{\underset{Pb}{<^O_O>}}{} Pb$, and the compound is regarded as the lead salt of an unstable orthoplumbic acid, $(HO)_4Pb$. This acid may be supposed to be the immediate product of the action of nitric acid on red lead:

$$Pb_2.PbO_4 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + H_4PbO_4;$$
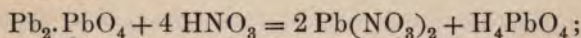
and, because of its instability, to break down at once into water and the dioxide. Similarly, the sesquioxide may be looked on as a metaplumbate, $Pb\underset{O}{\overset{O}{<\ >}}Pb=O$, a derivative of metaplumbic acid, $(HO)_2PbO$:

$$H_4PbO_4 - H_2O = H_2PbO_3.$$
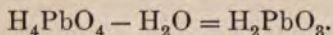
The monoxide turns moistened red litmus paper blue, as it forms some hydroxide, $Pb(OH)_2$. When fused with alkalies, alkaline earths, or other oxides of metals, it reacts with them to form a glass. It is used in making flint glass, glazes for pottery, and for the preparation of many lead compounds. Red lead finds large employment as paint. The dioxide is used to some extent as an oxidizing agent in the laboratory and as a constituent of match heads. It also plays an important part in the chemical changes of the storage battery in which elec-

trical energy is stored as chemical energy and then transformed into electrical energy again.

Lead Hydroxide, $Pb(OH)_2$, is precipitated from solutions of lead salts by caustic alkalies and dissolves in an excess with the formation of **plumbites**, such as Na_2PbO_2. Although the hydroxide thus appears as an acid towards strong bases, it is strongly basic towards acids, forming the one stable series of lead salts. The hydroxide is slightly soluble in water, and gives a faint alkaline reaction with litmus. It loses water easily and is converted at 145° into the monoxide.

Lead Nitrate, $Pb(NO_3)_2$, crystallizes as a white salt from solutions of lead, lead oxide, or carbonate, in nitric acid. The nitrate is readily made quantitatively from lead, and the figures which are obtained may be used to determine the equivalent of lead with reference to the known value for the nitric acid group NO_3. When heated, the salt decomposes, leaving a residue of the monoxide.

Lead Acetate, $Pb(CH_3CO.O)_2$, is made by the action of acetic acid on litharge. It crystallizes as $Pb(CH_3CO.O)_2,3\,H_2O$, and is very soluble. Its solutions have a sweetish taste and hence the salt is called "sugar of lead." The acetate and the nitrate are the salts of lead most commonly used, on account of their solubility. They are employed for the preparation of mordants, for making chrome yellow, and for some other minor uses.

Lead Carbonates; White Lead. — The normal carbonate of lead, $PbCO_3$, occurs in nature, and may be formed by precipitating lead nitrate with a soluble acid carbonate. When the normal carbonate of sodium is

added to a solution of a lead salt, a basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$, is precipitated. This substance, made in various ways, is the chief constituent of "white lead" which is so generally used for paint. The quality of the product, which is judged by its covering power, varies with the process of manufacture. The best white lead is made by the **Dutch method**. In this spirals of sheet lead, or gratings of cast lead, are placed in earthenware pots which contain some dilute acetic acid. The pots are loosely covered and placed in moist spent tanbark or other organic matter, which can be brought into fermentation. The heat of the fermenting material volatilizes the acetic acid, whose vapors act on the lead, forming basic lead acetate, and this is finally converted into the basic carbonate by the carbon dioxide produced in the fermentation. The process is a slow one, but it produces an amorphous white lead superior to the crystalline or granular products of other methods.

Lead Chlorides. — **Lead chloride,** $PbCl_2$, is only slightly soluble in cold water, and hence is precipitated when a soluble chloride is added to a solution of a lead salt. It is more soluble in hot water, most of it crystallizing out when a hot solution is cooled. A number of oxychlorides are known. Some of these occur as minerals, and two, called "Pattinson's white" and "Cassel yellow," have been used as pigments. **Lead tetrachloride,** $PbCl_4$, is an unstable yellow oily liquid. By leading chlorine into lead dichloride suspended in hydrochloric acid a solution of this substance is formed. On adding ammonium chloride a double salt, $PbCl_4,2\,NH_4Cl$, crystallizes out, from which the tetrachloride can be obtained by means of cold concentrated sulphuric acid. The tetra-

chloride resembles tin tetrachloride; it fumes in the air
and decomposes readily into the dichloride and chlorine.
When brought into a considerable amount of water, it is
hydrolyzed into hydrogen chloride and lead dioxide:

$$PbCl_4 + 2\,H_2O = PbO_2 + 4\,HCl.$$
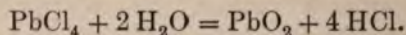
Lead Sulphate, $PbSO_4$, occurs as a mineral and is
readily made by precipitation, as it is almost completely
insoluble in water.   It differs from the insoluble barium
sulphate by being somewhat soluble in nitric acid and
in concentrated sodium hydroxide solution, and easily
soluble in ammonium tartrate.   It is slightly soluble
in concentrated sulphuric acid and hence is contained
in acid which has been concentrated in lead vessels.
When such acid is diluted, it becomes milky from the
precipitation of the lead sulphate.

Lead Sulphide, PbS, which as galena is the chief ore
of lead, is formed as a black precipitate when hydrogen
sulphide is passed into solutions of lead salts.   When
moist it oxidizes slowly in the air to sulphate, and is
readily converted into sulphate by strong nitric acid.

Lead Chromate, $PbCrO_4$, is precipitated from solutions
of lead salts by the alkali chromates.   It is made com-
mercially from lead nitrate or acetate, and is used as a
pigment, "chrome yellow."   By treatment with caustic
alkalies the chromate is converted into orange and red
basic chromates which are also employed as pigments.

Detection of Lead. — Lead is easily reduced from its
solid compounds by heating them with sodium carbonate
on charcoal.   The physical and chemical character of
the metal, and the appearance and behavior of the
chloride, sulphate, and chromate, precipitated from

solutions of lead salts, serve to identify this element. A simple test for lead in drinking water is the following : add to the water in a tall cylinder a little acetic acid and a very small quantity of finely powdered potassium dichromate.   Lead is shown by a yellow turbidity of lead chromate, and minute amounts are distinguished by placing the cylinder on a white surface and looking down through the liquid.

Quantitative Experiments. — Conversion of lead into chloride, nitrate, oxide, or sulphate; of the oxides of lead into lead or into the monoxide, chloride, nitrate, or sulphate ; of the nitrate into oxide, chloride, or sulphate ; of the sulphate into sulphide ; and of the sulphide into sulphate.   (See *Quantitative Experiments.*)

CHAPTER XXXI

COPPER

COPPER was the first metal employed for useful purposes. This is due to the fact that copper is found in nature in the metallic condition and thus can be utilized without further treatment. The displacement of copper from solutions of the naturally formed copper sulphate was apparently considered by the alchemists as a proof of the transmutation of metals.

Properties. — Copper is distinguished from all other metals by its color. The surface of polished copper reflects so much white light that the true red copper color is only seen when the light reaches the eye after repeated reflections, as from a piece of copper which has been bent at an acute angle. Copper is a very tough, malleable metal, and may readily be hammered into any shape, rolled to thin leaf, or drawn into fine wire. Copper melts at about the same temperature as gold. When heated out of contact with air, the melting point is 1084°; but in air, an oxide is formed which dissolves in the copper and lowers the melting point. Copper saturated with oxide melts at 1068°. At 2500° in the electric furnace copper can be distilled. It is unaltered in dry air, but in ordinary air it becomes dark from the formation of a film of basic carbonate which protects it from further corrosion. When heated

in air or oxygen, copper is converted into a black oxide; and it burns in sulphur vapor, forming a black sulphide. It does not act on water at any temperature and is hardly attacked by acids with the exception of nitric acid and hot concentrated sulphuric acid; but dilute acids, some salt solutions, and ammonia, together with oxygen of the air, act upon it slowly.

Copper is an excellent conductor of electricity, and very large amounts of the wire are used for electrical purposes. The properties of copper are much affected by the presence of even small amounts of impurities. Copper is used for roofing, sheathing ships' bottoms, making many kinds of vessels and stills, and as a component of important alloys, such as brass and various bronzes and coins.

Copper is less positive than most of the other metals, and is readily precipitated from its solutions by zinc, iron, and other more positive metals. Copper is both monovalent and divalent. The principal salts are those of divalent copper.

Occurrence. — Copper occurs in the metallic state to some extent, sometimes in large masses. It is also found in combination as oxide, carbonate, and sulphide, often with sulphides and arsenides of iron and other metals. Copper is also found in plants growing in copper-bearing localities; in the feathers of some birds; and in the blood of some mollusks, such as the cuttle-fish, whose arterial blood is blue, and contains copper compounds which appear to play the same part that compounds of iron do in the red blood of most animals.

Extraction. — The extraction of copper from the oxide and carbonate ores is readily effected by reduction with

coal and proper fluxes.   The treatment of the sulphide
ores is more elaborate because of the difficulty of sepa-
rating copper from sulphur, for which its affinity is much
stronger than is that of iron.   By repeated roastings
and smeltings with fluxes, the iron is oxidized and re-
moved in the slag, and a fairly pure copper sulphide,
called " white metal," is obtained.   This is then partly
reduced by an " air reduction process " as in the case of
lead sulphide (p. 356), and the crude copper purified
by a further smelting process ; or the reduction is carried
out in converters, like those used in the Bessemer pro-
cess, with a blast of air and a siliceous lining to serve as
a flux for the iron oxide which is produced.   Poor ores
and burnt pyrites from sulphuric acid works are roasted
with rock salt.   By this operation the copper is con-
verted into a soluble chloride from which the copper is
precipitated by scrap iron.

The demand for a high degree of purity in the cop-
per used for electrical purposes is met by a process of
electrolytic refining.   In this, slabs of copper from the
smelting process are made the anodes in a bath of
copper sulphate and sulphuric acid, the cathodes being
thin sheets of pure copper.   By the action of the elec-
tric current, pure copper is deposited on the cathodes
and dissolved from the anode.   The less positive metals,
such as gold, silver, antimony, etc., which are in the
crude copper, fall to the bottom of the bath, forming a
mud from which they may be recovered ; while the
more positive metals, such as iron, zinc, etc., are dis-
solved and remain in solution.

Copper Sulphate, $CuSO_4$. — This is the most important
compound of copper.   It is well known and extensively

used under the name of " blue vitriol." It is found in
the drainage of copper mines, and is obtained commer-
cially by roasting copper pyrites, dissolving the copper
sulphate which is formed, and crystallizing it from the
solution. The crystals usually contain some iron sul-
phate — green vitriol — from the iron in the pyrites.
Copper sulphate is also made from copper and dilute
sulphuric acid with the oxidizing aid of the air or of
nitric acid. The action of hot concentrated sulphuric
acid on copper gives, as the chief products, copper sul-
phate and sulphur dioxide (p. 91).

Copper sulphate is much more soluble in hot than in
cold water, and crystallizes from its solutions in fine blue
crystals which have the composition $CuSO_4,5 H_2O$.
These crystals effloresce slightly in dry air, and at 100°
lose four fifths of their water, leaving a bluish white
powder of $CuSO_4,H_2O$. Traces of water are retained
by the salt up to the temperature at which it begins to
decompose, but at 200° it is practically anhydrous and
white. The anhydrous salt is very hygroscopic and be-
comes blue as it takes up water. On this account it is
sometimes used to detect the presence of water in or-
ganic liquids, such as absolute alcohol, and to render
them anhydrous.

Copper sulphate is used as the starting point for mak-
ing other copper compounds ; its solution is employed
as a battery fluid, in copper-plating, as a mordant in
dyeing, and as a germicide and insecticide in spraying
plants and trees. The much used " Bordeaux mixture "
is a mixture of copper sulphate and milk of lime. Small
amounts of copper sulphate are found effective in de-
stroying certain algæ which appear in reservoirs of

water supplies and impart a disagreeable taste and odor to the water.

Copper Nitrate, $Cu(NO_3)_2$, is made by dissolving copper in nitric acid. Its solutions yield deliquescent blue crystals, $Cu(NO_3)_2,6\,H_2O$, which are partly hydrolyzed when heated, and consequently the anhydrous normal salt cannot be obtained. The basic salt which is produced by heating the crystals is easily decomposed at a higher temperature, leaving black copper oxide. Copper nitrate finds some use as an oxidizing agent in dyeing and calico printing.

Copper Chlorides. — When copper is heated in chlorine, cupric chloride, $CuCl_2$, is formed. By the action of a mixture of hydrochloric acid with some nitric acid this chloride is also produced, and can be obtained from its solution in deliquescent blue crystals of the composition $CuCl_2,2\,H_2O$. At 100° these crystals lose their water and the brown anhydrous chloride is formed, which, on further heating, loses chlorine and is converted into cuprous chloride. The anhydrous salt is brown.

Cuprous chloride, $CuCl$, is a white substance, insoluble in water, but soluble in hydrochloric acid and in ammonia. These solutions oxidize when exposed to the air, with the formation of cupric compounds. They absorb carbon monoxide and acetylene with the precipitation of unstable compounds formed with these gases, and are used for this purpose in gas analysis.

Cuprous chloride is easily prepared by a number of methods all of which depend on reductions of cupric chloride. Two methods which are often employed are:
1. By boiling a hydrochloric acid solution of cupric

chloride with copper turnings. The cuprous chloride produced is dissolved in the hydrochloric acid, and may be precipitated by pouring the solution into a large amount of water. 2. By leading sulphur dioxide into a solution of copper sulphate and common salt; cuprous chloride is precipitated.

Copper bromides corresponding to the two chlorides are obtained by similar methods. Cupric iodide is not known, **cuprous iodide**, CuI, being precipitated from solutions of cupric salts on addition of potassium iodide or other soluble iodides, iodine separating at the same time:

$$2\,CuSO_4 + 4\,KI = 2\,K_2SO_4 + 2\,CuI + I_2.$$
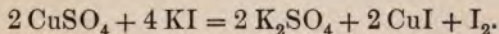
Copper Oxides and Hydroxides. — Cupric hydroxide, $Cu(OH)_2$, is probably present in the light blue precipitate which is produced when potassium or sodium hydroxide is added to a solution of a cupric salt. The gelatinous precipitate is converted, by boiling the mixture, into a black cupric oxyhydroxide. The hydroxide dissolves readily in ammonia, forming a deep blue solution which is thus obtained when ammonia is added in excess to a cupric solution. From the solution of the precipitate in ammonia, the normal hydroxide, $Cu(OH)_2$, is separated by adding an excess of a strong solution of potassium or sodium hydroxide. It is a blue powder which is easily washed free from alkali. It is stable even in boiling water. On heating this hydroxide, or the gelatinous precipitate, both are converted into black cupric oxide, CuO. No cuprous hydroxide of the formula CuOH is known.

Cupric oxide, CuO, is also formed when copper is heated

2 B

in oxygen, but the oxidation is not complete unless the copper is in the conditon of fine powder. The black scale which falls from hot copper when hammered is a mixture of the two oxides. Cupric oxide begins to lose oxygen above 360° with the formation of Cu_2O, and at 2500° in the electric furnace is completely decomposed into copper and oxygen. It is readily reduced when heated with hydrogen, carbon, or any compound of carbon, and is used in the analysis of organic substances to oxidize their hydrogen to water and their carbon to carbon dioxide, from whose weight the amount of hydrogen and carbon in the substances is calculated.

Cuprous oxide, Cu_2O, is one of the minerals of copper, and may be formed by the reduction of cupric compounds.   When glucose and sodium hydroxide are added to a solution of copper sulphate, a clear, dark blue solution is obtained, which gives, on heating, a red precipitate of cuprous oxide, formed by the reducing action of the glucose. This production of cuprous oxide by reducing sugars is made the basis of a method for determining the amount of such sugars in solutions. Cuprous oxide gives cuprous chloride with hydrochloric acid, but with dilute sulphuric or nitric acids cupric salts and copper are formed :

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$
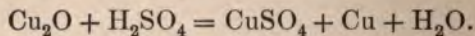
Copper Sulphides. — There are two sulphides of copper corresponding to the two oxides. That which is produced by burning copper in sulphur vapor is the **cuprous sulphide**, Cu_2S. **Cupric sulphide**, CuS, can be formed by *heating* cuprous sulphide with sulphur at its boiling

point. It is also precipitated from cupric solutions by hydrogen sulphide. When moist it oxidizes rather easily, and when heated in a current of hydrogen it gives Cu_2S, which is not reduced further. Both of the sulphides occur naturally; and it is the more stable cuprous sulphide which plays such an important part in the extraction of copper from its ores.

Other Compounds of Copper. — No normal carbonate of copper can be made. A **basic carbonate**, malachite, occurs naturally, and is precipitated when soluble carbonates are added to cupric salts. **Cupric cyanide,** $Cu(CN)_2$, is precipitated when potassium cyanide is added to a solution of a cupric salt, but it immediately decomposes into cyanogen gas and **cuprous cyanide,** CuCN. This forms a soluble double salt with an excess of potassium cyanide, and from these solutions the usual reagents fail to precipitate copper compounds, complex ions being formed. This fact is useful in separating copper from other metals in analytical work. **Copper acetate** is obtained as a basic salt — "verdigris" — by the action of acetic acid and air on copper. It is used in making "paris green," an aceto-arsenite of copper, which although of a fine green color is little used as a pigment on account of its poisonous character, and is chiefly used as an insecticide.

The deep blue solution obtained by dissolving copper hydroxide in ammonia, "Schweitzer's reagent," is a solvent for cellulose (filter paper, cotton, etc.), which is precipitated from the solution unchanged when an acid is added.

A large number of complex compounds are formed by the action of ammonia on the salts of copper.

Detection of Copper. — Copper is detected in its solid compounds by their reduction to the metal when heated with sodium carbonate before the blowpipe. When brought into solution as cupric compounds, the color of the solution and the dark blue produced by an excess of ammonia are characteristic. Metallic copper is readily precipitated upon zinc or iron from solutions of its salts, and recognized by its color. The chloride and nitrate color the flame green, and this flame coloration is obtained from other compounds when moistened with hydrochloric acid. All copper compounds color the borax bead in the oxidizing flame, green while hot, and blue when cold; in the reducing flame the bead becomes red and opaque.

Quantitative Experiments. — Conversion of copper into oxide, sulphide, chloride, or sulphate; of cupric sulphide into cuprous sulphide; of the sulphate into oxide; and reduction of either oxide or the sulphate to copper. (See *Quantitative Experiments.*)

CHAPTER XXXII

MERCURY AND SILVER

MERCURY

THOUGH mercury was not known as early as some other metals, it appears in the records at least 300 years before the Christian era, and a mine in Spain which is still producing the metal has been worked since that time. Its Latin name, hydrargyrum, and the common name, "quicksilver," both describe it as liquid silver.

Properties. — It is the only useful metal which is liquid at ordinary temperatures. At about $-39°$ it becomes solid, and in this form is malleable and ductile. At $357°$ it boils, and the density of its vapor indicates that in this state the molecules consist of single atoms. It is the heaviest of the well-known metals with the exception of gold and platinum, having a specific gravity of about 13.6. The surface tension of mercury is so great that, in spite of its weight, small drops have an almost spherical form. It dissolves all familiar metals except iron and platinum, forming amalgams which may be either liquid or solid, according to the amount of mercury they contain.

Mercury does not oxidize at ordinary temperatures, but when heated in air to a temperature just below its boiling point, a red oxide is slowly formed. The oxidation of mercury in this manner is of great historical

interest (p. 14). When heated with sulphur it combines with it, and it unites directly with the halogens. Towards acids, mercury behaves like copper. It is dissolved only by nitric acid or hot concentrated sulphuric acid. Mercury is precipitated from solutions of its compounds by copper and all the metals which precede it in the electromotive series.

Uses. — Mercury is used in barometers and manometers because it is a heavy liquid and has a very low vapor tension. The range of mercury thermometers is limited by the freezing and boiling points of the mercury; but the upper limit may be extended by filling the space above the mercury with nitrogen, which has no chemical action on it, and raises its boiling point by the increased pressure produced as the mercury rises. Gases which dissolve in water are often collected over mercury for experimental purposes. Mercury is also used in extracting gold and silver from their ores as amalgams, as a cathode substance in certain electrolytic processes, for making amalgams, and as the source of the various mercury compounds.

Mercury may be obtained in a state of extremely fine division by rubbing it with various powders, and is used in this form in medicine ("blue mass").

Occurrence and Extraction. — Mercury occurs free in small amounts and is found amalgamated with gold and silver. Its most important ore is the sulphide, cinnabar, which is found in comparatively few localities, the chief mines being in Spain, California, and Bavaria. The metal is obtained by roasting the ore in a current of air, or heating it with lime in a retort. In both cases the mercury distils off and is condensed in receivers. The

mechanical impurities, such as soot, etc., are removed
from the mercury by filtration through cloth or leather.
The commercial mercury usually contains small amounts
of other metals in solution.   These give a black powder
when the mercury is shaken with air, and cause it to
leave a "tail" when it is poured.   Mercury may be puri-
fied from metals which are more positive than itself
by treating it with dilute nitric acid or other oxidizing
solutions, and it can be purified from all other metals by
distillation in vacuum.

Compounds of Mercury. — Mercury, like copper, forms
two series of compounds, the mercurous and the mer-
curic.   In the mercuric compounds, molecular weight
determinations show that mercury acts as a dyad.   For
the mercurous compounds the evidence is not so con-
clusive, but, as in the case of cuprous compounds, the
mercurous compounds are usually represented as con-
taining monad mercury, as in $HgCl$.   Formulas such as
Hg_2Cl_2 or $Cl-Hg-Hg-Cl$, in which mercury is a dyad,
are also in use.   Until a final decision is reached, it seems
best to use the simpler formulas.

All of the compounds of mercury, like those of am-
monium, are volatilized when heated, those containing
oxygen or cyanogen being decomposed, and the others
subliming without decomposition.   Light acts on mer-
cury compounds as on silver compounds, but in less
degree.   Mercury vapor and all of the compounds of
mercury are poisonous; the toxic action of the insoluble
compounds being naturally less than that of those which
are soluble.

The chief soluble salt of mercury is the mercuric
chloride.   It is very slightly hydrolyzed.   Mercuric

cyanide is also readily soluble, being an exception in this respect to the cyanides of the other heavy metals. Mercuric and mercurous nitrates and sulphates are decomposed by water into insoluble basic salts, and clear solutions of these salts are obtained only by the addition of acids. The halides of mercury, both mercuric and mercurous, are insoluble or very sparingly soluble in water, except mercuric chloride. The fluorides are hydrolyzed. All the compounds of mercury are readily reduced from the mercuric to the mercurous condition or to mercury.

Nitrates. — **Mercurous nitrate,** $HgNO_3$, is made by the action of cold dilute nitric acid on an excess of mercury. It crystallizes as $HgNO_3, H_2O$. In its solution in nitric acid the tendency to oxidize into mercuric nitrate is counteracted by keeping some mercury in the bottle.

By action of hot, strong nitric acid in excess on mercury or mercurous nitrate, a solution of **mercuric nitrate,** $Hg(NO_3)_2$, is formed, from which deliquescent crystals containing water of hydration can be obtained.

Sulphates. — **Mercurous sulphate,** Hg_2SO_4, is so slightly soluble in water that the mercury in a mercurous nitrate solution is almost completely precipitated as sulphate on the addition of sulphuric acid. **Mercuric sulphate,** $HgSO_4$, is made by the action of an excess of hot concentrated sulphuric acid on mercury. When it is heated, it breaks up into mercury, oxygen, sulphur dioxide, and mercurous sulphate, and the last at a higher temperature gives mercury, oxygen, and sulphur dioxide.

Halides. — **Mercurous chloride,** $HgCl$, is a heavy, white, *nearly* insoluble powder. It may be formed by the

action of chlorine on an excess of mercury, and is obtained as a precipitate when soluble chlorides are added to solutions of mercurous salts, and by the reduction of mercuric chloride. It is usually prepared by sublimation from a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg = 2\,HgCl.$$
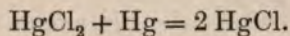
Mercurous chloride sublimes without melting. In the state of vapor it is partly dissociated into mercury and mercuric chloride, which, on cooling, unite to form mercurous chloride again (compare with the behavior of ammonium chloride, p. 148). It is used in medicine under the name of "calomel." Light acts on it slowly with the formation of the mercuric salt. Ammonia changes it into a black substance.

Mercuric chloride, $HgCl_2$, commonly known as "corrosive sublimate," may be formed by the action of an excess of chlorine on mercury or on mercurous chloride, or by dissolving mercury in aqua regia. The usual method of preparation is by heating an intimate mixture of mercuric sulphate and common salt. The chloride sublimes and forms a crystalline mass. It is soluble in water and in alcohol, and is very poisonous. Solutions of mercuric chloride are easily reduced to mercurous chloride and this to mercury. A reaction of analytical importance is that with stannous chloride (p. 351).

It is used as a preservative for skins and to prevent decay of wood. It is also employed to destroy vermin, and very dilute solutions are used in surgery to disinfect wounds and to render the hands and instruments aseptic.

The **iodides** can both be obtained by rubbing mercury and iodine together in the proper proportions, or by precipitation of mercury solutions by potassium iodide. The precipitate of **mercurous iodide**, HgI, is greenish yellow, and decomposes readily into mercury and **mercuric iodide**, HgI_2. The latter, when precipitated from a solution of mercuric chloride, is yellow at first, but soon changes to scarlet.

The mercuric halides form compound salts with the corresponding halides of potassium, sodium, and ammonium, which are more soluble than the mercury salts alone.   A solution of potassium mercuric iodide containing potassium hydroxide is a very delicate test for ammonia and ammonium salts, traces of which turn it yellowish brown.   This solution is known as " Nessler's reagent ". (p. 150).   The white precipitate obtained by adding ammonium hydroxide to a mercuric chloride solution has the formula $NHgH_2Cl$, which appears to be an ammonium salt in which two hydrogen atoms are replaced by a dyad atom of mercury.   The black substance produced by ammonia with mercurous chloride is a mixture of this compound and mercury.

Other Compounds of Mercury. — The hydroxides of mercury are too unstable to exist.   The precipitates which are formed when caustic alkalies are added to mercurous and mercuric salts are the oxides.   **Mercurous oxide**, Hg_2O, is a dark-colored powder which readily decomposes into mercuric oxide and mercury. Precipitated **mercuric oxide**, HgO, is yellow, while that formed by oxidizing mercury is red.   The red oxide is usually prepared by heating mercuric nitrate, mixed *with* mercury, till no more red vapors are given off.

The oxide is decomposed by heat into mercury and oxygen.

Mercuric Sulphide, HgS (mercurous sulphide does not exist), is the chief ore of mercury. It may be formed by precipitation of mercury salts with hydrogen sulphide, or by rubbing together mercury and sulphur. In both cases it is black and amorphous. On standing under a warm solution of potassium sulphide, or by subliming the dry sulphide, it is obtained as a red crystalline substance known as " vermilion," and used as a pigment in oil and water colors, in printer's ink, and in sealing wax. Both the black and red varieties are insoluble in single acids, even in boiling nitric acid. They dissolve, however, in aqua regia, forming mercuric chloride.

Mercurous Carbonate may be precipitated from mercurous solutions as a yellow powder which darkens in the light, and decomposes at 130°. Only basic mercuric carbonates are known.

Mercuric Cyanide, $Hg(CN)_2$, is the only cyanide of a heavy metal which is soluble in water. It is made by dissolving precipitated mercuric oxide in hydrocyanic acid, or by boiling a solution of mercuric sulphate and potassium ferrocyanide. The crystalline salt decomposes, when heated, into mercury and cyanogen, and is used for the preparation of this gas. Its solutions fail to give some of the reactions of other soluble mercuric salts, which is explained by the very slight dissociation of the cyanide in solution.

Mercuric Thiocyanate, $Hg(SCN)_2$, is precipitated from mercuric solutions by potassium thiocyanate, KSCN, as a white powder. When this is formed into small balls

and ignited, it burns with the production of a very vo-
luminous vermiform ash, (Pharaoh's serpents).   **Mer-
cury fulminate**, $Hg(ONC)_2$, is produced when mercury
is dissolved in nitric acid in the presence of alcohol.
When the white powder is dry, it explodes easily on
being struck, and is used for percussion caps, and as
a detonating substance for firing dynamite and gun
cotton.

Detection of Mercury. — Heated with sodium carbonate
in an ignition tube, all compounds of mercury give off
the metal, and this condenses in droplets on the cool
walls of the tube.   Mercury is precipitated on a bright
strip of copper brought into its solution, and may be
deposited on copper or on platinum by electrolysis.
Solutions of mercurous salts are precipitated by hydro-
chloric acid, and the mercurous chloride turns black
with ammonia.   Mercurous chloride and mercury are
precipitated from mercuric solutions by stannous chlo-
ride (p. 351).

Quantitative Experiments. — Conversion of mercury
into oxide or sulphate ; of mercuric oxide into mercury
and oxygen.   (See *Quantitative Experiments.*)

SILVER

Properties. — Silver is a very white metal which in
thin leaf transmits blue light.   It is rather soft and of
great ductility and malleability.   It is the best con-
ductor of electricity known.   It melts at 962°.   Silver
combines slightly with oxygen at very high tempera-
tures ; but when melted it dissolves about twenty-four
times its volume of oxygen, and this is nearly all ex-
pelled when it solidifies.   The oxygen as it escapes

through the crust which forms on the cooling metal often carries silver with it.

Silver combines readily with sulphur when heated with it, and hydrogen sulphide in moist air produces a dark film of silver sulphide.   This is the principal cause of the tarnishing of silverware.   Hydrochloric acid attacks silver very slightly ; hot, concentrated sulphuric acid dissolves it with evolution of sulphur dioxide; and nitric acid readily converts it into the soluble nitrate.   Alkalies, whether in solution or melted, have no action on silver, and hence silver vessels are used in the laboratory for heating alkaline substances, in place of vessels of platinum, since platinum is attacked by these reagents.   Silver alloys readily with other metals and dissolves in mercury.

Almost all commercial silver is alloyed with copper to render it harder and more durable.   The silver coinage of the United States, Germany, and France, contains 10 per cent of copper, and that of Great Britain, 7.5 per cent.   Silver ornaments contain 80 per cent or more of silver.   When these alloys are heated in air, and the copper oxide which is thus formed is dissolved by dilute sulphuric acid, a layer of almost pure silver is left which presents a " frosted " appearance until it is burnished. " Oxidized " silver is silver tarnished by a film of silver sulphide, produced by dipping the silver article into a solution of an alkaline sulphide.

Much silver is used for plating on other metals, usually by electrolysis.   The electroplating bath is a solution of the double cyanide of silver and potassium.   A coherent film of silver can be deposited on glass by the reduction of ammoniacal silver solutions by various

organic substances, such as aldehyde, glucose, or alkaline tartrates.   This process is used for making mirrors, having supplanted the former method of pressing an amalgam of tin and mercury on the glass.   The silvered mirrors are more brilliant and more durable than those made with the amalgam.

Silver acts only as a monovalent element.

Occurrence and Extraction. — Silver occurs to some extent in the metallic state, but native silver is usually alloyed with gold or copper.   Its most important ore is the sulphide, either by itself, or in double sulphides with other metals, and the chloride.   The occurrence of silver in galena, the chief ore of lead, has already been noted.   The processes of extraction vary with the character of the ore and its richness in silver, as well as with local conditions in regard to cost of fuel, etc. They may be classified as : *dry methods*, whose immediate object is to obtain an alloy of silver and lead ; *amalgamation methods*, in which native silver, or the metal set free in the process, is amalgamated with mercury ; and *wet methods*, by which compounds of silver are brought into solution and the silver is then precipitated by copper.

Alloys with lead are obtained by smelting the ore with the addition of lead, if this metal is not already present in the ore in sufficient quantity.   The lead is then removed by oxidation (cupellation).   As already noticed, most lead ores contain silver in small amounts, and the silver which is in the lead after reduction of the ore is concentrated in zinc or a smaller amount of lead by methods which have been described (p. 357). The lead alloy is treated as above, and the zinc is re-

moved by distillation with lime and coal as in the extraction of zinc.

In the amalgamation methods, the silver compounds of the ore are converted into silver chloride, and this is reduced by mercury, an excess of mercury dissolving the silver as it is set free. A process of this kind has been used for 350 years in Mexico and involves some interesting reactions. The finely ground ore is thoroughly incorporated with salt and water, and to the mud thus obtained ferric and cupric sulphates and mercury are added, and the whole trodden by mules for several weeks. The chlorides of iron and copper are formed by reaction of the sulphates with the salt, and reacting in turn with the silver ore (sulphide) produce silver chloride :

$$Ag_2S + 2\,CuCl_2 = 2\,AgCl + 2\,CuCl + S\,;$$
$$\text{and}\quad Ag_2S + 2\,CuCl\ = 2\,AgCl + Cu_2S.$$
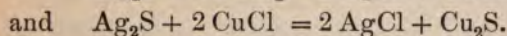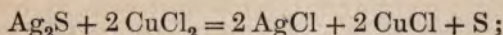
The silver chloride dissolves in the strong solution of salt and is reduced by the mercury :

$$AgCl + Hg = Ag + HgCl,$$
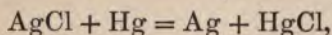
and the silver is dissolved in the excess of mercury. When the operation is completed, the heavy amalgam is freed from the lighter substances by washing, and is filtered through canvas. Finally the mercury is distilled from the silver.

In the methods which convert the silver into soluble salts from which it is precipitated by metallic copper, the silver is usually changed into the soluble sulphate by careful roasting of the sulphide ores, or to chloride by roasting with salt. The sulphate is soluble in water, and

the chloride is dissolved in a saturated solution of salt or in a solution of sodium thiosulphate. Silver is separated from gold and platinum by treatment with hot concentrated sulphuric acid or dilute nitric acid. The noble metals remain undissolved and the silver is precipitated by iron. Crude silver is also refined by electrolysis in a manner similar to that employed for copper. The bath is a solution of silver nitrate made acid with nitric acid, and the crystalline silver which separates on the cathode is rubbed off mechanically as it forms, in order to prevent short-circuiting of the electric current.

Silver can be obtained from its alloys with copper as follows : The alloy is dissolved in nitric acid and the silver precipitated by hydrochloric acid. The solid chloride is washed free from copper salts and is then reduced by placing zinc in contact with it. The silver obtained in this way is a gray powder, called **molecular silver.**

Silver Nitrate, $AgNO_3$, is the most important soluble compound of silver and the starting point for making the other compounds. It is made by the action of nitric acid on silver. The anhydrous nitrate is crystallized from the solution, or the solution is evaporated to dryness and the nitrate fused and cast in small sticks. Silver nitrate may also be prepared from the commercial alloys of silver and copper by evaporating the solution in nitric acid, and heating till the copper nitrate is all decomposed to oxide. The unchanged silver nitrate is then dissolved and crystallized.

Silver nitrate melts at 191° and decomposes at a red heat, leaving a residue of metallic silver. Some silver

is, however, lost in this operation unless a reducing agent,
such as charcoal, is present. Silver nitrate is blackened
by organic matter on exposure to light because of its
ready reduction to metallic silver. It is used on this
account in certain indelible inks. Silver nitrate is a
powerful caustic, and sticks of it are used in surgery ·
under the name of " lunar caustic." Its solutions are
precipitated by sodium or potassium hydroxides, by
soluble halides, and by hydrogen sulphide. Metallic
silver is separated from the nitrate solution by all the
common metals except gold and platinum. Ammonia,
added in excess, gives a solution from which crystals of
the complex salt $AgNO_3$, $2\,NH_3$ can be obtained.

Silver Halides. — The chloride, AgCl, bromide, AgBr,
and iodide, AgI, are all insoluble salts which may be
made from solutions of silver nitrate by adding the
corresponding soluble halides. They form curdy pre-
cipitates which darken on exposure to light and are
insoluble in nitric acid. The chloride is white, the
others yellow. They are all soluble in ammonia, alka-
line cyanides, and thiosulphates, the solubility diminish-
ing very much from chloride to iodide. They also
dissolve in the corresponding alkaline halides. The
silver halides are all acted on by light, the action being
favored by contact with an organic substance. This
behavior is the basis of photography.

Photography. — The sensitive layer on the modern
dry plate or film consists of gelatine in which particles
of silver bromide are embedded. The gelatine is
melted and silver bromide precipitated in it by addition
of silver nitrate and ammonium bromide. After heat-
ing for some time to produce finely divided bromide,

2 c

which gives greater sensitiveness to light, the "emulsion" is allowed to cool and become solid. It is then cut into small pieces and the ammonium nitrate formed in the reaction is washed out. The gelatine is now remelted and flowed on to the glass plate or celluloid sheet which serves as a support. Exposure in the camera produces no visible change in the appearance, but in the "developer," which is a reducing agent, the parts which were affected by the light darken in proportion as the illumination of the part was greater. When the development has proceeded far enough, the bromide which is still unchanged is removed by a solution of sodium thiosulphate ("hypo") so that no further change can occur when the plate is exposed to light ("fixing"). The "negative" which results presents a picture of the object with the shading reversed, and is used to produce positive prints by placing it over sensitized paper and exposing to light. The papers used for photographic printing are of many varieties. They may be covered with a film of material which, like that of the plate, requires only a short exposure and is then developed, or with a substance like silver chloride which is darkened by longer exposure to light. The color of the print is corrected or changed by "toning" it with solutions of gold or platinum salts which replace part of the reduced silver with these metals. (For blue prints see p. 341.)

There is considerable uncertainty as to the chemical change produced by the camera exposure, but the developer reduces the slightly changed bromide to metallic silver, and it is this which forms the image. The gelatine not only serves as a means for holding the

silver bromide and the reduction products in place, but promotes the action of the light, which would be very slight in the bromide alone.

Other Compounds of Silver. — **Silver monoxide,** Ag_2O, is obtained as a pale brown powder when the precipitate by an alkali in a solution of silver nitrate is dried at a temperature below 100°. The hydroxide, AgOH, is unstable and apparently not formed. The oxide is readily decomposed by heat into silver and oxygen. A black compound which separates on the anode in the electrolysis of silver nitrate solutions, and which has been called silver peroxide, is a complex compound of the composition Ag_7NO_{11}. On boiling this compound with water the **peroxide,** Ag_2O_2, is precipitated.

Silver Sulphide, Ag_2S, is one of the chief ores of silver. It may be made by heating silver with sulphur, and is formed as a black precipitate from silver solutions by hydrogen sulphide. Heated in the air, it gives sulphur dioxide, silver, and a little silver sulphate. It is reduced to silver by hydrogen at a red heat.

Silver Sulphate, Ag_2SO_4, is formed by the action of hot concentrated sulphuric acid on silver. It is decomposed by heat into silver, sulphur dioxide, and oxygen, and is readily reduced by hydrogen or carbon to silver. It is sparingly soluble in water. With aluminium sulphate a silver alum is formed, $AgAl(SO_4)_2, 12 H_2O$.

Silver Carbonate, Ag_2CO_3 (yellowish), the **Phosphate,** Ag_3PO_4 (yellow), **Arsenate,** Ag_3AsO_4 (brown), and **Chromate,** Ag_2CrO_4 (red), are precipitated by the soluble salts of the corresponding acids. They are all soluble in nitric acid.

The silver salts resemble the cuprous salts in their

general insolubility. The soluble salts are not hydrolyzed in solution and basic salts are not formed. In this respect the silver compounds are like the salts of the most positive metals, though silver stands nearly at the bottom of the electromotive series, is displaced from its solutions by almost all other metals, and forms an unstable oxide. Like copper again, silver enters into many complex compounds, most of the salts of silver being soluble in ammonia with the formation of such compounds. Most of the silver salts are also soluble in sodium thiosulphate and in potassium cyanide from the production of soluble double salts.

Detection of Silver. — Silver is readily detected. Its solid compounds are all readily reduced to metallic silver by fusion with sodium carbonate on charcoal before the blowpipe. In solution, silver is recognized by the precipitation of the chloride which is soluble in ammonia and insoluble in nitric acid.

Quantitative Experiments. — Conversion of silver into the halides, nitrate, sulphate, or sulphide ; of the oxide into iodide, nitrate, or silver ; of the nitrate into the halides, sulphate, or silver ; and of the sulphate or sulphide into silver. (See *Quantitative Experiments.*)

CHAPTER XXXIII

GOLD AND PLATINUM

GOLD

GOLD was probably the first metal known, as it is widely distributed, and almost always occurs in the metallic state, requiring no treatment for extraction beyond the mechanical separation from the sand or rock in which it is found. On account of its fine color and its unalterability, it has always been prized for ornamental purposes and used as the standard of values. Gold leaf and the film of gold on plated ware are pure gold; but in gold coins and the gold used for jewelry, etc., the gold is always alloyed with copper or silver, or with both these metals, to render it harder and stronger.

It is usual to express the proportion of gold in the alloys employed for gold ware and for ornaments in "carats," 24-carat gold being pure gold. Thus 14-carat gold, which is frequently used, is an alloy containing 14 parts of gold and 10 parts of copper. The gold coins of the United States, Germany, and France are of the same "fineness" as the silver coins of these countries, containing 90 per cent of gold; while the English gold coinage has a fineness of 916.67 parts of gold to 1,000, being 22-carat gold.

Properties. — Gold is distinguished from all other elementary metals by its color. It is one of the heaviest

substances known, having a specific gravity of 19.3, and is the most malleable and ductile of all metals.   It can be beaten into leaf which is only one ten-thousandth of a millimeter thick, and one gram of the finest gold wire has a length of more than three thousand meters.

Gold is unalterable in the air and is not attacked by any single acid except selenic acid, and very slightly by boiling strong nitric acid.   It dissolves in aqua regia, and in any solution which contains free chlorine or bromine.   It is also dissolved by alkaline cyanides in the presence of air, and in sulphuric acid on addition of certain oxidizing agents, such as potassium permanganate.   Fused nitrates attack it and also fused caustic alkalies with the aid of the oxygen of the air.   Gold is the most electropositive of the metals and its compounds have little stability.   They are readily decomposed by heat, leaving a residue of the metal; and gold is precipitated from their solutions by all other metals and by reducing agents, and even by charcoal.

Gold acts as a monad and as a triad in compounds which are called aurous and auric respectively.

Halogen Compounds.—By the action of chlorine in solution, and by the action of aqua regia, gold gives a solution from which deliquescent yellow crystals may be obtained of **chlorauric acid**, $HAuCl_4 (= HCl, AuCl_3)$, $4 H_2O$.   On gentle heating, this becomes **auric chloride**, $AuCl_3$, a red, deliquescent salt, which is changed at about 200° into a white, insoluble powder of **aurous chloride**, $AuCl$.   At higher temperatures aurous chloride decomposes into chlorine and gold, and in boiling water into auric chloride and gold.   **Sodium chloraurate**, $NaAuCl_4$, $2 H_2O$, is a yellow salt used in photography for toning prints.

The bromine compounds of gold are similar to the chlorine compounds, but are even less stable. **Aurous iodide**, AuI, is precipitated by potassium iodide from a solution of chlorauric acid or of its salts, auric iodide being very unstable.

Other Compounds of Gold. — Potassium or sodium hydroxides precipitate from solutions of chlorauric acid or its salts, brownish **auric hydroxide**, $Au(OH)_3$, which dissolves in excess of the alkali, giving salts which correspond to a **metauric acid**, $HAuO_2$. By careful heating the hydroxide is converted into **auric oxide**, Au_2O_3, which breaks up very readily on further heating into gold and oxygen. Ammonia precipitates from auric solutions a very explosive compound, known as **fulminating gold**, $2 AuN_2H_3, 3 H_2O$. The same substance is obtained pure by the action of concentrated ammonia on auric hydroxide. **Aurous hydroxide**, $AuOH$, and **aurous oxide**, Au_2O, are both very unstable compounds. **Aurous sulphide**, Au_2S, is precipitated by hydrogen sulphide both from aurous and auric solutions, mixed in the latter case with sulphur and some auric sulphide. The sulphides are soluble in solutions of alkali sulphides, giving sulphaurites and sulphaurates.

The double cyanides of gold and potassium or sodium are important, as they furnish the best solutions for the electro-deposition of gold, as in gold plating; and because the formation of the soluble aurous cyanides, by the action of dilute alkali cyanide solutions on gold in the presence of air, is largely utilized in the extraction of gold from its ores.

The Purple of Cassius is a finely divided precipitate obtained by adding stannous chloride containing a little

stannic chloride to auric solutions, and is believed to be a "lake" of tin oxide colored by finely divided gold. It is used in making ruby glass and as a color in porcelain painting; and also serves as a test for gold in solution.

Extraction of Gold. — Though native gold is very widely distributed, the amount is often too small to repay the cost of its extraction. It occurs in many rocks, and often in pyrites and in some other minerals; but is generally found in quartz veins or reefs, and in the sands, gravels, and clays which have resulted from the natural disintegration of gold-bearing rocks. Though nuggets of considerable size are sometimes found, most of the gold is in small grains or scales, or in a still more finely divided state. The only important compounds of gold found in nature are those in which it is combined with tellurium, either alone or with other metals, chiefly silver. The gold is set free from the tellurides by roasting the ore, so that the chief problem of extraction from the various sources is that of separating the small amounts of metallic gold from the other substances with which it is more or less intimately mixed. When the gold is in loose sand or gravel, its high specific gravity makes it possible to effect a separation by agitating the material with running water. This method is made more effective by the use of mercury, which dissolves and holds the finer particles that would otherwise be washed away. This principle is employed in various ways, from the simple pan-washing or cradling to the hydraulic mining, in which the gravel is broken up by powerful jets of water and washed down long sluices containing pockets

partly filled with mercury. In quartz mining, the gold-bearing quartz is crushed in stamping mills, and the gold extracted from the fine material by washing it over amalgamated copper plates. The gold is finally obtained from the amalgam by distillation of the mercury.

Small amounts of gold which escape the amalgamation process can be extracted by the *cyanide process*. This consists in treating the material with a very dilute solution of potassium cyanide. With the aid of the oxygen of the air this dissolves the gold as a double cyanide:

$$4\,Au + 8\,KCN + 2\,H_2O + O_2 = 4\,KOH + 4\,KAu(CN)_2;$$
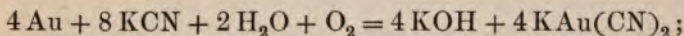
and the gold is then precipitated from the cyanide solution by zinc shavings:

$$2\,KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2\,Au,$$
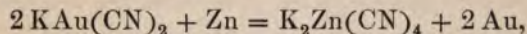
or deposited by electrolysis on lead cathodes and afterwards obtained by cupellation.

Still another method, which is used for extracting gold from pyrites, depends on the direct action of chlorine on gold. The roasted pyrites is washed, and then treated with chlorine. In the presence of water the gold is converted into the soluble auric chloride and is then precipitated from its solution by reducing agents such as ferrous sulphate.

$$AuCl_3 + 3\,FeSO_4 = FeCl_3 + Fe_2(SO_4)_3 + Au.$$
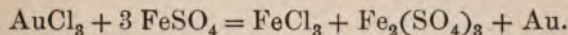
The gold which is extracted from its ore in these ways contains silver and often other metals, in varying quantities, which sometimes amount to from 10 to 15 per cent. Various methods are employed for

refining the crude gold.   If oxidizable metals, such as
lead, iron, antimony, etc., are present in any consider-
able amount, the metal is usually melted with borax
and saltpeter.   The oxides which are formed rise to
the top of the molten metal and are removed, leaving
an alloy of gold and silver.

The separation of gold and silver ("parting") may
be effected by nitric or concentrated sulphuric acids,
but only when the alloy contains one third or less of
its weight of gold.   It may, therefore, be necessary to
melt the gold-silver alloy with enough silver to give this
proportion before making the separation.   Another
method consists in passing a stream of chlorine through
the melted alloy.   The temperature is much above the
decomposition temperature of gold chloride, so that
this is not formed; the chloride of silver collects as a
liquid layer on the surface, and is afterwards reduced
to silver, while the chlorides of zinc, antimony, bis-
muth, and arsenic, if these metals were present, are
volatilized.

A considerable quantity of gold is obtained as a by-
product from the residue of pyrites used in the manu-
facture of sulphuric acid; from the mud precipitated
in the electrolytic refining of copper; and in other
metallurgical operations.   The United States, the
Transvaal, and Australasia, each produce about one
quarter of the annual output of gold.

Detection of Gold. — This metal is recognized by its
color, malleability, and behavior towards solvents, and
is readily obtained from its compounds by heating with
sodium carbonate before the blowpipe, or precipitated
from its solutions by other metals or reducing agents.

METALS OF THE PLATINUM GROUP

This group of metals contains six members: ruthenium, rhodium, palladium, osmium, iridium, and platinum. They generally occur together in natural alloys, which also contain gold, copper, and iron, in grains and occasionally in larger masses in alluvial sands. The heavy ore is separated from the sand by washing with water, as in placer gold mining.

PLATINUM

Extraction. — Platinum, which is by far the most important metal of the group, is obtained by the following process: The ore is treated repeatedly with aqua regia. The solution contains platinum, iridium, ruthenium, rhodium, usually some palladium, and the metals of the other groups. The residue consists of osmium and iridium with some ruthenium. From this solution of the chlorides, platinum and iridium are precipitated by ammonium chloride as double salts, which on ignition leave the metals as a spongy mass. This is made into compact metal by heating and hammering. The amount of iridium in the metal thus obtained is about two per cent, and as this alloy of platinum and iridium is more resistant to chemical action than pure platinum, further purification is usually omitted.

Properties. — Platinum is a grayish white metal. It is only less ductile than gold and silver. A small amount of iridium renders it harder and less ductile.

It is the heaviest of the useful metals, having a specific gravity of 21.5. Its melting point is far higher than

that of gold.   Before melting, it becomes soft and can be welded, and as it does not oxidize, no flux is necessary.   It forms alloys with all metals, when heated with them to about their melting points.   In the compact state it does not amalgamate with mercury.   Chlorine in solution attacks it slightly.   Silicon and phosphorus combine with it and render it brittle, and it is attacked by fused caustic alkalies and by alkaline nitrates, sulphides, and cyanides.   It is insoluble in any single acid.

Platinum sponge, which is obtained by the ignition of the double chloride of platinum and ammonium, and **platinum black**, a fine black powder, precipitated from platinum solutions by reducing agents such as aluminium, zinc, etc., condense gases on their surface and act as efficient contact agents in causing various chemical reactions (ignition of hydrogen (p. 66), synthesis of sulphur trioxide (pp. 84, 85).   Even a spiral of fine platinum wire, or a piece of thin foil, when heated, may cause certain reactions to take place, such as the oxidation of ammonia, or of alcohol vapor.   The extensive use of platinum crucibles, dishes, wire, etc., in laboratory operations depends on the chemically inactive character of this metal and on its high melting point. Its employment must be avoided whenever any of the few substances which act on it are to be used, or formed in the reactions.   Platinum is used for electrical contacts in electrical instruments, and short lengths of platinum wire fused in the glass of incandescent electric lamps convey the current to the filament within.   This last use depends on the fact that platinum is the only metal which has the same coefficient of expansion as *glass*.

COMPOUNDS OF PLATINUM

Platinum forms two series of compounds, the **platinous**, in which it is a dyad, and the **platinic**, in which it is a tetrad.

Choroplatinic Acid, $H_2PtCl_6,6\,H_2O$, crystallizes as a reddish brown, deliquescent salt from the solution of platinum in aqua regia. Its potassium and ammonium salts, K_2PtCl_6 and $(NH_4)_2PtCl_6$, are only slightly soluble in water and are insoluble in alcohol. They are useful on this account in making analytical separations. When heated, the crystals of chloroplatinic acid lose both water and hydrogen chloride, and without yielding either the anhydrous acid or platinic chloride, give at 360° **platinous chloride**, $PtCl_2$, which at higher temperatures decomposes completely. **Platinic chloride**, $PtCl_4$, may be obtained by heating chloroplatinic acid to 275° in chlorine. It decomposes when heated, first into platinous chloride and chlorine, and then gives metallic platinum. The other compounds of platinum, the hydroxides, oxides, and sulphides, corresponding to the two chlorides, are unstable and of slight importance. All platinum compounds are completely decomposed by heat.

Detection of Platinum. — All compounds of platinum are readily reduced. The platinum is soluble in aqua regia and from this solution potassium or ammonium chloride precipitates the crystalline yellow chloroplatinates, which are less soluble in alcohol than in water. The dark-colored sulphides are precipitated from platinum solutions in the presence of acids, and like the sulphides of gold, tin, arsenic, and antimony are soluble in yellow ammonium sulphide.

THE OTHER METALS OF THE PLATINUM GROUP

Osmium and iridium have specific gravities of about 22.5, being the heaviest of all metals, while the specific gravities of ruthenium, rhodium, and palladium are only a little more than half as large. The melting points of all except palladium are higher than that of platinum, osmium and ruthenium being the most infusible of all metals. Ruthenium, osmium, and iridium are hard and brittle, rhodium is ductile and malleable at a red heat, and palladium resembles platinum in its hardness, ductility, and malleability. Osmium, ruthenium, and rhodium are oxidized when heated in air or oxygen. Palladium dissolves in nitric acid and osmium is oxidized by this acid. Ruthenium, rhodium, and iridium, when pure, are insoluble in all acids, but in the form of alloys dissolve somewhat in aqua regia. They may be brought into solution by the action of a fused mixture of alkali hydroxide and nitrate.

Palladium has the property of absorbing hydrogen in large amount. The amount of hydrogen which is taken up varies with the state of the metal and other conditions. Compact palladium, obtained by electrolysis, when heated to 100° and allowed to cool in the gas, absorbs nearly 1000 times its volume. Palladium charged with hydrogen acts as a reducing agent, precipitating copper from solutions of its salts, changing ferric to ferrous salts, etc. The hydrogen is all driven off at a red heat.

Osmium Tetroxide, OsO_4, is a white crystalline substance formed by burning osmium, or by treating it with nitric acid. It melts at 40° and boils at 100°, and

is soluble in water. Though not an acid anhydride, it is commonly called osmic acid. It vaporizes somewhat at ordinary temperatures, emitting an acrid vapor which attacks the eyes dangerously. It is used for staining and hardening microscopic preparations in histology.

The metals which are associated with platinum are at present of little practical importance. Iridium or an alloy of osmium and iridium is used for the tips of gold pens. An alloy of platinum with a little iridium is commonly employed for platinum utensils; and a very hard, elastic alloy containing more iridium has been used for making standard meter bars and for electrodes in corrosive liquids. Pure rhodium is said to be used for crucibles, etc.

CHAPTER XXXIV

THE PERIODIC SYSTEM; SOME RARE ELEMENTS

THE PERIODIC SYSTEM

A RELATION between the properties of certain elements and their atomic weights has been noticed in our study of several natural groups, — that of the halogens, of phosphorus, arsenic, and antimony, of the metals of the alkalies, and of the metals of the alkaline earths.

In 1869 Mendeléef published a classification of the elements, which included all that were known, and revealed a general relationship between the properties and the atomic weights.

When the elements are arranged in the order of increasing atomic weights, it is found that the tenth, neon, repeats the properties of the second, helium; that the eleventh, sodium, resembles the third, lithium; and so on up to the seventeenth, chlorine, which is closely related to the ninth, fluorine. That is, beginning with helium, similar properties are repeated in every eighth element to the seventeenth.

If a table is made to show these relations, and similar elements are placed in vertical columns, it is seen that the regularity, which appears in the first two horizontal lines, is by no means complete. In the table on the opposite page, argon is placed under neon, and potassium under sodium, because of the obvious simi-

PERIODIC SYSTEM OF THE ELEMENTS

Series	Group 0	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII RO_4
1	—	H=1.008	—	—					—
2	He=4	Li=7	Gl=9.1	B=11	C=12	N=14	O=16	F=19	—
3	Ne=20	Na=23	Mg=24.8	Al=27.1	Si=28.8	P=31	S=32.1	Cl=35.5	—
4	A=39.9	K=39.1	Ca=40.1	Sc=44.1	Ti=48.1	V=51.2	Cr=52	Mn=54.9	Fe=55.8 Ni=58.7 Co=59
5	—	Cu=63.6	Zn=65.4	Ga=69.9	Ge=72.5	As=75	Se=79.2	Br=79.9	—
6	Kr=88	Rb=85.5	Sr=87.6	Y=89	Zr=90.6	Cb=93.5	Mo=96	—	Ru=101.7 Rh=102.9 Pd=106.7
7	—	Ag=107.9	Cd=112.4	In=114.8	Sn=119	Sb=120.2	Te=127.5	I=126.9	—
8	Xe=130.7	Cs=132.8	Ba=137.4	La=189	Ce=140.2	—	—	—	—
9	—	—	—	Yb=172	—	—	—	—	—
10	—	—	—	—	—	Ta=181	W=184	—	Os=190.9 Ir=193.1 Pt=195
11	—	Au=197.2	Hg=200	Tl=204	Pb=207.1	Bi=208	—	—	—
12	—	—	Ra=226.4	—	Th=232.4	—	U=238.5	—	—

larities, though the atomic weight order would reverse these positions.   For like reasons the places of tellurium and iodine are reversed.   Further, to bring the elements from calcium to bromine into their natural groups, iron, nickel, and cobalt must be placed in a new group and a blank left under argon.   A number of such adjustments are necessary ; and if hydrogen is to be brought into the system, it must stand in Group I, though it does not present any marked relationship to the metals of this group.

The blanks which are left in carrying out this arrangement may be supposed to belong to elements which are still undiscovered.   Indeed, when Mendeléef first published the classification, a place was left between calcium and titanium, and two places between zinc and arsenic; and he predicted the atomic weights and the properties of the elements which should fill them.   In less than twenty years these predictions were brilliantly fulfilled by the discovery of gallium (1875), scandium (1879), and germanium (1886).

In Groups I–VII of the table we find the base-forming elements at the left and the acid-forming elements at the right, with a gradation from the most strongly basic in Group I to the most strongly acidic in Group VII.   The maximum valence of the elements of each group towards oxygen increases from one to seven and eight, while the valence towards hydrogen decreases from four in Group IV to one in Group VII.   The maximum oxygen valences are indicated by the group numbers and also by typical formulas in which " R " stands for a monad metal.   The valence of the helium group, whose members form no compounds, is called

zero. After the series or periods numbered 2 and 3, it will be noticed that sub-groups are indicated by the positions of the symbols in the vertical columns. For instance, in Group II, calcium, strontium, and barium, which form a natural family, are placed at the left, while glucinum, magnesium, zinc, and cadmium, which are more closely related to each other than to the metals of the alkaline earths, are at the right. Further discussion of this classification would be out of place here, but it may be stated that, in general, *the properties of the elements are periodic (or recurrent) functions of the atomic weights.*

While the classification shows a number of irregularities and is by no means satisfactory, it brings out clearly the fact that there is evidently a connection between the properties and the atomic weights ; and we may regard the present system as foreshadowing the discovery of a more exact natural law.

For a century the idea that the chemical elements are merely very stable compounds of one or more primordial substances has frequently recurred. The periodic relationship of the elements lends some color to this view ; and further, the probable breaking down of some of the elements of largest atomic weights, such as uranium and radium, into other elements, seems to point in the same direction.

SOME RARE ELEMENTS

The general relationships of the elements which have not been discussed in the preceding pages may be seen by their positions in the periodic system. A few of them are of sufficient general interest or importance to

justify brief statements in description of their proper-
ties and uses.

Selenium and Tellurium are two elements which re-
semble sulphur in their general nature and behavior.
Selenium occurs in some specimens of sulphur, but both
selenium and tellurium are found chiefly in combination
with metals.   They form gaseous compounds with hy-
drogen, which are like hydrogen sulphide, though less
stable.   They burn to dioxides, which are solids.   The
dioxide of selenium is freely soluble in water and the
solution gives crystals of selenious acid, H_2SeO_3.   Tel-
lurium oxide is almost completely insoluble.   Both ele-
ments form acids which are analogous to sulphuric acid.
Both can be obtained in several allotropic states.   One
form of selenium, a gray, semi-metallic substance, con-
ducts electricity slightly, and this property, which is
increased by light in proportion to the intensity of the
illumination, has been made the basis of attempts to
telephone, etc., by means of beams of light.

Metals of the Rare Earths. — Some fifteen elements
which are very closely related and very difficult to
separate from each other, so that the elementary char-
acter of some of them has been long in doubt, are known
as the metals of the rare earths.   Their atomic weights
lie between those of cerium, 140.25, and tantalum, 181,
and their position in the periodic system is uncertain.
They are usually divided into three groups: the **cerium
group**, which includes cerium, scandium, yttrium, lan-
thanum, praseodymium, neodymium, and samarium;
the **terbium group**, terbium, europium, and gadolinium;
and the **ytterbium group**, dysprosium, holmium, erbium,
thulium, neoytterbium, and lutecium.   **Thorium** occurs

with cerium and other rare earth metals, and its oxide is the chief constituent of the mantle of the Welsbach lamp. With the growth of the Welsbach industry, large amounts of the rare earths have been obtained as by-product, and this has supplied abundant material for the investigation of the rare earth puzzle. In the manufacture of the **Welsbach mantle,** a loosely knitted sleeve of cotton thread, of the form of the mantle, is dipped into a solution of the nitrates of thorium and cerium. The mantle is then dried and ignited, with the result that a coherent but fragile skeleton of the oxides of the metals is left, which, in the lamp, is heated by a Bunsen burner. It is a singular fact that the presence of a small amount of cerium oxide is necessary for the greatest efficiency. It acts, perhaps, as a contact agent, causing a more rapid combustion of the gas, and, therefore, a higher temperature.

In the Nernst lamp, a rod consisting of several oxides of these earths is heated to incandescence by the electric current. The rod conducts the current only when warm, so the current first passes through a wire coiled about the rod, and, when this is heated, is automatically shunted to pass through the rod.

Molybdenum is related to chromium. **Ammonium molybdate,** $(NH_4)_2MoO_4$, is an important reagent in analytical chemistry. It gives a characteristic precipitate with nitric acid solutions of phosphates or phosphoric acid, which serves for the detection and separation of the phosphoric acid group. **Tungsten** and **uranium** are also members of the chromium group. The most important ore of tungsten is wolframite, and the symbol of the element is W. Metallic tungsten forms the fila-

ment in the efficient tungsten electric lamp, and sodium tungstate is used as a mordant and for fireproofing cloth.   Uranium is found chiefly in the mineral pitchblende.   Its compounds are used in making uranium glass, which has a yellowish fluorescence.

Alloys of iron with molybdenum, tungsten, vanadium, and titanium are prepared commercially, and are used in steel making.

Radium.—Compounds of this element were discovered by M. and Mme. Curie in 1898 in pitchblende.   It occurs in such small amounts that only a few tenths of a gram of radium salts are obtained from a ton of the residues left after pitchblende has been worked for uranium.   The extraction is very tedious and costly, and only a few grams of radium salts have thus far been produced.   Chemically, radium compounds resemble those of barium.   The isolation of the metal by Mme. Curie from an amalgam formed in the electrolysis of its bromide with a mercury cathode has recently been reported.   The chief interest in radium compounds is because of their remarkable **radioactivity**.   It is this property which led to their discovery.   Radium salts are continually giving out energy.   They maintain themselves at a temperature from $3°$ to $5°$ above the surrounding air, and from them proceed invisible rays which produce phosphorescent and photographic effects, and render the air a conductor, so that electroscopes are discharged.   Some of the rays penetrate opaque objects. A gradual disintegration of radium is supposed to be going on, and helium has been recognized as one of its products.   Uranium and thorium are also radioactive, but in a very much less degree than radium.

APPENDIX

I

THE METRIC SYSTEM OF WEIGHTS AND MEASURES

In this system the standards are: for length, the **meter**; for volume, the **liter**; and for weight, the **gram**. It is a decimal system, and the multiples and divisions of the standards are designated by prefixes. The prefixes of the multiples are Greek, *deca-* = 10, *hecto-* = 100, and *kilo-* = 1000. Thus 1000 grams = 100 decagrams = 10 hectograms = 1 kilogram. The prefixes of the divisions are Latin, *deci-* = 0.1, *centi-* = 0.01, and *milli-* = 0.001. Thus 1 gram = 10 decigrams = 100 centigrams = 1000 milligrams.

The weights and the measures of the metric system are related to each other as follows: The liter = 0.001 cubic meter = 1 cubic decimeter = 1000 cubic centimeters; and the gram is the weight of 1 cubic centimeter of pure water at 4° C. (the temperature of its greatest density). One liter of water, therefore, weighs 1000 grams or 1 kilogram.

The units which are most frequently used are: for length, the **meter** (m.), the **centimeter** (cm.), and the **millimeter** (mm.); for volume, the **liter** (l.), and the **cubic centimeter** (cc.), parts of a liter being expressed in cubic centimeters rather than in the decimal divisions of the

liter; for weight, the **kilogram** (kg.), the **gram** (g.), and the **milligram** (mg.).

The relation of the metric units to those in common use is shown in the following table:

TABLE OF EQUIVALENT WEIGHTS AND MEASURES

1 meter	= 39.37 inches.	1 foot	= 30.48 cm.
1 centimeter	= 0.3937 inches.	1 inch	= 2.54 cm.
1 liter	= 1.0567 U.S. quarts.	1 U.S. quart	= 0.946 l.
1 kilogram	= 2.2 lb. avoir.	1 U.S. liquid oz.	= 29.574 cc.
1 kilogram	= 2.68 lb. troy.	1 lb. avoir.	= 453.59 g.
1 gram	= 15.43 grains.	1 lb. troy	= 373.24 g.
1 gram	= 0.035 oz. avoir.	1 oz. avoir.	= 28.35 g.
1 gram	= 0.032 oz. troy.	1 oz. troy	= 31.1 g.
		1 grain	= 64.8 mg.

II

THE MEASUREMENT OF TEMPERATURE

In the ordinary mercury thermometer the scale is constructed with reference to two temperatures which

212° F. | 100° C.
80° R. | 373° A.

can be easily reproduced. One is the temperature of melting ice, and the other that of the steam from water

32° F. | 0° C.
0° R. | 273° A.

boiling under the standard pressure of 760 mm. or 29.92 inches of mercury. In the **Fahrenheit** thermometer, commonly used for household and meteorological purposes, these points are marked 32° and 212° respectively, the space between being divided into 180

− 459.4° F. | − 273° C.
− 218.4° R. | 0° A.

degrees. In the **centigrade** thermometer, the melting point is 0° and the boiling

point 100°, with 100 degrees between. In the **Réaumur** thermometer, which is commonly used in Germany, the fixed points are 0° and 80°. Thus 180 degrees of the Fahrenheit scale are equal to 100 degrees centigrade or 80 degrees Réaumur, and the reading of one scale may be converted into the equivalent in the other scales as follows:

To change Fahrenheit to centigrade, subtract 32 and multiply by $\frac{5}{9}$; centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32. Or

$$°C. = \tfrac{5}{9}(°F. - 32); \qquad °F. = \tfrac{9}{5}°C. + 32.$$

The change from Réaumur to Fahrenheit or centigrade, or from these scales to Réaumur is made thus:

$$°C. = \tfrac{5}{4}°R.; \;\; °F. = \tfrac{9}{4}°R. + 32; \;\; °R. = \tfrac{4}{5}°C. = \tfrac{4}{9}(°F. - 32).$$

" **Absolute** " temperatures are given in centigrade degrees, the zero being transferred to $-273°$ C. The absolute temperature is, therefore, equal to the temperature centigrade plus 273.

As mercury freezes at 38.8° C. and boils at 357° C., temperatures outside of this range cannot be determined by the ordinary mercury thermometer. Thermometers in which the space above the mercury is filled with nitrogen can be used for much higher temperatures; and alcohol or pentane thermometers serve for lower temperatures. Temperatures extending over a much wider range are determined by air or gas thermometers; by means of the change in electrical resistance which is shown by metals with change of temperature; by the electric current produced when one junction of a circuit of two metals is at a different temperature from the other; and in various other indirect ways.

The highest temperature which can be produced is that of the electric arc between carbon terminals, — about 3500° C. It cannot be exceeded, because carbon volatilizes at that temperature. Low temperatures are produced by the evaporation of liquefied gases, especially when their boiling points are lowered by reduced pressure. The boiling point of helium is − 268.7° C., only 4.3° above the absolute zero.

High temperatures are often roughly described in terms of the color of the light which is emitted by strongly heated bodies. The approximate temperatures in centigrade degrees which correspond to the different colors is given in the following table:

COLOR SCALE OF TEMPERATURE

Faint Red . . . . . 500°	Orange . . . . 1100°
Dull Red . . . . . 700°	Bright Orange . . . 1200°
Bright Red . . . . . 800°	White . . . . . . 1300°
Cherry Red . . . . . 900°	Bright White . . . . 1400°
Bright Cherry . . . . 1000°	

III

TENSION OF AQUEOUS VAPOR IN MILLIMETERS OF MERCURY

°C.	TENSION	°C.	TENSION	°C.	TENSION	°C.	TENSION
0.0	4.6	14.0	11.9	18.5	15.8	23.0	20.9
10.0	9.2	14.5	12.3	19.0	16.3	23.5	21.5
10.5	9.5	15.0	12.7	19.5	16.9	24.0	22.2
11.0	9.8	15.5	13.1	20.0	17.4	24.5	22.9
11.5	10.1	16.0	13.5	20.5	17.9	25.0	23.6
12.0	10.5	16.5	14.0	21.0	18.5	25.5	24.3
12.5	10.8	17.0	14.4	21.5	19.1	26.0	25.0
13.0	11.2	17.5	14.9	22.0	19.7	26.5	25.7
13.5	11.5	18.0	15.4	22.5	20.3	27.0	26.5

IV

CRITICAL TEMPERATURES, CRITICAL PRESSURES, AND BOILING POINTS OF SOME GASES

The critical temperature of a gas is that temperature to which the gas must be cooled before it can be liquefied by any pressure, however great. The critical pressure is the pressure necessary to liquefy a gas at its critical temperature. The boiling points given in the table are those of the liquefied gases under atmospheric pressure. The critical pressures are given in atmospheres.

	CRITICAL TEMPER-ATURE	CRITICAL PRES-SURE	BOILING POINT
Helium . . .	—	—	$-268.7°$
Hydrogen . .	$-242°$	15	-252.5
Neon . . .	-210	—	$-243-233$
Nitrogen . . .	-149	28	-195.5
Carbon Monoxide .	-136	36	-190
Oxygen . . .	-119	58	-182.5
Argon . . .	-117.4	53	-186.1
Nitric Oxide . .	-93.5	71	-149.9
Methane . . .	—	—	-155
Krypton . . .	-62.5	54	-157.7
Xenon . . .	14.8	57	-109.1
Carbon Dioxide .	31	73	-78.2
Acetylene . .	35	55	-82.5
Nitrous Oxide . .	37	77	-89.8
Hydrogen Chloride .	52.3	86	-80
Hydrogen Sulphide .	100	90	-61.8
Cyanogen . .	124	62	-20.7
Ammonia . .	131	83	-38.5
Chlorine . . .	146	93.5	-33.6
Sulphur Dioxide .	155.4	79	-8
Steam . . .	370	195	100

V

THE SPECIFIC GRAVITY OF GASES AND THE WEIGHT OF ONE LITER

(UNDER STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE, AT LATITUDE 41° AND AT SEA LEVEL)

	SPECIFIC GRAVITIES		WEIGHTS OF ONE LITER		MOLECULAR WEIGHTS
	Observed Values	Theoretical Values	Observed Values	Theoretical Values	
Air	1.0000	——	1.2923	——	——
Hydrogen . . .	0.06926	0.06965	0.0895	0.0900	2.016
Helium	0.1368	0.1382	0.1768	0.1786	4.0
Ammonia . . .	0.5971	0.5885	0.7716	0.76055	17.034
Neon	0.674	0.691	0.871	0.893	20.0
Hydrogen Fluoride	0.7126	0.691	0.921	0.893	20.008
Acetylene . . .	0.92	0.8988	1.1889	1.1615	26.016
Carbon Monoxide .	0.9670	0.9673	1.2499	1.2501	28.0
Nitrogen . . .	0.9672	0.9701	1.2499	1.2537	28.02
Nitric Oxide . .	1.0372	1.0378	1.3406	1.3412	30.01
Oxygen	1.10535	1.1055	1.4285	1.4287	32.0
Hydrogen Sulphide	1.1895	1.1773	1.5372	1.5215	34.086
Hydrogen Chloride	1.2692	1.2595	1.6402	1.6276	36.468
Fluorine	1.26	1.313	1.628	1.697	38.0
Argon	1.379	1.379	1.782	1.782	39.9
Carbon Dioxide .	1.5291	1.5201	1.9761	1.9645	44.0
Nitrous Oxide . .	1.5301	1.5229	1.9777	1.9681	44.02
Cyanogen . . .	1.8064	1.7993	2.3344	2.3252	52.02
Sulphur Dioxide .	2.2639	2.2131	2.9257	2.8600	64.07
Chlorine	2.491	2.4494	3.2192	3.1654	70.92
Hydrogen Bromide	2.71	2.7973	3.502	3.615	80.928
Krypton	2.8676	2.8680	3.7060	3.7065	83.0
Hydrogen Iodide .	4.376	4.417	5.655	5.708	127.928
Xenon	4.5147	4.5153	5.8345	5.8353	130.7

VI

SOLUBILITY OF GASES IN WATER

The figures give the normal volume of the gases which dissolve in one volume of water at the temperature indicated.

	0°	20°
Helium	0.0150	0.0139
Hydrogen	0.0215	0.0182
Nitrogen	0.0235	0.0154
Air	0.0288	0.0187
Carbon Monoxide	0.0354	0.0232
Oxygen	0.0489	0.0310
Argon	0.0578	0.0379
Nitric Oxide	0.0738	0.0471
Nitrous Oxide	1.048 (5°)	0.629
Carbon Dioxide	1.713	0.878
Chlorine	4.610	2.260
Hydrogen Sulphide	4.686	2.672
Sulphur Dioxide	79.79	39.37
Hydrogen Chloride	506.5	442.0
Ammonia	1298.9	710.6

VII

TABLE OF SOLUBILITIES

The figures in this table give the weight of the anhydrous substance in grams which dissolves in 100 grams of water at the indicated temperatures. The data are taken from Seidell's *Solubilities of Inorganic and Organic Substances*.

TABLE OF SOLUBILITIES

	20°	100°
Aluminium Sulphate . . .	36.1	89.1
Ammonia Alum	7.74	109.7 (95°)
Potassium Alum	5.9	119.0 (92.5°)
Ammonium Chloride . . .	37.2	77.3
Ammonium Nitrate . . .	192.4	871
Ammonium Sulphate . . .	75.4	103.3
Barium Chloride	35.7	58.8
Barium Hydroxide . . .	3.89	101.4 (80°)
Barium Nitrate	9.2	34.2
Boric Acid	4.0	27.5
Bromine	3.58	——
Cadmium Sulphate . . .	76.6	60.77
Calcium Chloride	91.0	159
Calcium Hydroxide . . .	0.16	0.08
Chlorine	0.73	0.00
Copper Sulphate	20.7	75.4
Ferric Chloride	91.85	535.8
Ferrous Sulphate	26.42	43.0 (90°)
Lead Chloride	0.91 (15°)	3.34
Lead Iodide	0.06 (15°)	0.44
Lead Nitrate	52.3	127
Lithium Carbonate . . .	1.33	0.72
Lithium Chloride	78.5	127.5
Lithium Sulphate . . .	25.5	23.0
Magnesium Chloride . . .	54.5	73
Magnesium Sulphate . . .	36.2	73.8
Manganese Sulphate . . .	61.08 (15°)	32.0
Nickel Sulphate	37.9 (22.6°)	76.71 (99°)
Potassium Bromide . . .	62.5	104.0
Potassium Carbonate . . .	112.0	156.0
Potassium Chlorate . . .	7.22	55.54
Potassium Chloride . . .	34.0	56.7

TABLE OF SOLUBILITIES — *Continued*

	20°	100°
Potassium Chromate . . .	61.7	75.6
Potassium Dichromate . . .	12.0	80.0
Potassium Hydroxide . . .	112	178
Potassium Iodide	144	208
Potassium Nitrate . . .	31.6	246
Potassium Sulphate . . .	11.11	24.1
Silver Nitrate	222	952
Sodium Borate (Borax) . .	2.8 (21.5°)	52.5
Sodium Carbonate . . .	21.5	45.5
Sodium Dicarbonate . . .	9.6	16.4 (60°)
Sodium Chloride	36.0	39.8
Sodium Hydroxide . . .	109	365 (110°)
Sodium Nitrate	88	180
Sodium Sulphate	19.4	42.5
Sodium Thiosulphate . . .	70.07	174.2
Strontium Chloride . . .	52.9	100.8
Strontium Nitrate . . .	70.8	101.1
Zinc Chloride	396	615
Zinc Sulphate	50.88	80.8

VIII

THE RELATIVE HARDNESS OF THE ELEMENTS

A scale of hardness used by the mineralogists and consisting of ten minerals, ranging from talc, the softest, to the diamond, the hardest, has been used for indicating the relative hardness of the elements.[1] In the following table the principal solid elements are arranged in the order of increasing hardness on this scale.

[1] J. R. Rydberg, "Zeitschrift für physikalische Chemie," **33**, 353.

THE RELATIVE HARDNESS OF THE ELEMENTS

Cæsium	0.2	Sulphur	2.0	Antimony	3.0
Rubidium	0.3	Selenium	2.0	Arsenic	3.5
Sodium	0.4	Magnesium	2.0	Platinum	4.3
Potassium	0.5	Cadmium	2.0	Iron	4.5
Phosphorus	0.5	Barium	2.0	Palladium	4.8
Lithium	0.6	Tellurium	2.3	Cobalt	5.0
Iodine	0.8	Zinc	2.5	Nickel	5.0
Mercury (solid)	1.5	Bismuth	2.5	Manganese	6.0
Calcium	1.5	Gold	2.5	Iridium	6.5
Lead	1.5	Silver	2.7	Silicon	7.0
Tin	1.8	Aluminium	2.9	Chromium	9.0
Strontium	1.8	Copper	3.0	Carbon	10.0

IX

THE SPECIFIC GRAVITIES OF THE ELEMENTS

Lithium	0.534	Antimony	6.62
Potassium	0.863	Zinc	6.86–7.3
Sodium	0.972	Chromium	6.9
Chlorine (liquid)	1.44	Tin (white)	7.29
Rubidium	1.53	Manganese	7.49
Calcium	1.52	Iron	7.86
Magnesium	1.74	Molybdenum	8.6
Phosphorus (white)	1.83	Cadmium	8.64
Cæsium	1.87	Cobalt	8.7
Sulphur (monocl.)	1.96	Nickel	8.8
Sulphur (rhomb.)	2.05–2.07	Copper	8.95
Phosphorus (red)	2.11	Bismuth	9.8
Carbon (graphite)	2.01–2.58	Silver	10.50
Silicon (cryst.)	2.49	Lead	11.38
Strontium	2.54	Palladium	11.4
Boron (cryst.)	2.68	Rhodium	12.1
Aluminium	2.6	Ruthenium	12.26
Bromine	3.15	Mercury	13.59
Titanium	3.54	Uranium	18.7
Barium	3.75–4.0	Tungsten	19.1
Selenium (met.)	4.8	Gold	19.32
Iodine	4.95	Platinum	21.5
Arsenic	5.73	Iridium	22.4
Tin (gray)	5.8	Osmium	22.48
Tellurium	6.27		

X

MELTING POINTS OF THE ELEMENTS

Non-Metals	Metals	Metals
Hydrogen . . $-258.9°$	Mercury $-38.8°$	Barium $850°$
Fluorine . . . $-233°$	Cæsium . $26.5°$	Silver . . . $961.5°$
Oxygen . . . $-223°$	Rubidium $38.5°$	Gold . . . $1065°$
Nitrogen . . $-210.5°$	Potassium $62.5°$	Copper . . $1084°$
Chlorine . . $-102°$	Sodium . $95.6°$	Manganese . $1245°$
Bromine . . . $-7.3°$	Lithium . $186°$	Nickel . . $1484°$
Phosphorus . . $44.3°$	Tin . . . $232°$	Chromium . $1515°$
Iodine . . . $114.2°$	Bismuth . $269°$	Cobalt . . $1530°$
Sulphur (rhomb.) $114.5°$	Cadmium . $322°$	Palladium . $1550°$
Sulphur (monocl.) $119.2°$	Lead . . $327°$	Platinum 1710–$1780°$
Selenium . . . $217°$	Zinc . . $419°$	Iron, pure . $1804°$
Tellurium . . $452°$	Antimony $630°$	Iron, wrought $1600°$
Arsenic . . . $500°$	Magnesium $632.6°$	Steel . . . $1375°$
Silicon . . . $1200°$	Aluminium $657°$	Iron, gray pig $1275°$
	Calcium . $800°$	Iron, white pig $1075°$

XI

THE SPECIFIC AND ATOMIC HEATS OF SOME OF THE SOLID ELEMENTS

	Specific Heat	Atomic Weight	Atomic Heat
Aluminium	.222	27.1	6.0
Antimony	.0495	120.2	5.9
Bismuth	.03013	208.0	6.3
Cadmium	.0548	112.4	6.1
Chromium	.10394	52.0	5.4
Cobalt	.1030	58.97	6.1
Copper	.0936	63.57	5.9
Gold	.0316	197.2	6.2
Iron	.1162	55.85	6.5
Lead	.0310	207.1	6.4
Magnesium	.2456	24.32	6.0
Manganese	.1217	54.93	6.7

2 E

THE SPECIFIC AND ATOMIC HEATS OF SOME OF THE SOLID ELEMENTS—*Continued*

	Specific Heat	Atomic Weight	Atomic Heat
Mercury	.03346	200.0	6.7
Nickel	.1084	58.68	6.4
Platinum	.0323	195.0	6.3
Silver	.0559	107.88	6.0

.XI

RELATIVE ABUNDANCE OF THE ELEMENTS

	Earth's Crust	Oceans	Average Including the Air
Oxygen	47.07	85.79	49.78
Silicon	28.06		26.08
Aluminium	7.90		7.34
Iron	4.43		4.11
Calcium	3.44	.05	3.19
Sodium	2.43	1.14	2.33
Potassium	2.45	.04	2.28
Magnesium	2.40	.14	2.24
Hydrogen	.22	10.67	.95
Titanium	.40		.37
Chlorine	.07	2.07	.21
Carbon	.20	.002	.19
Sulphur	.11		.11
Phosphorus	.11		.11
Barium	.09		.09
Manganese	.07		.07
Strontium	.03		.03
Nitrogen			.02
Fluorine	.02		.02
Bromine		.008	
All other elements	.50		.48
	100.00	100.00	100.00

XII

DISCOVERY OF THE ELEMENTS

The dates are those of the first recognition of the element as a new substance, except in some cases where the date of its isolation is given.

Gold	Pre-historic	Chromium	1797
Silver	Pre-historic	Glucinum	1797
Copper	Pre-historic	Yttrium	1797
Tin	Pre-historic	Tellurium	1798
Lead	Pre-historic	Columbium	1801
Iron	Pre-historic	Tantalum	1802
Mercury	Pre-historic	Palladium	1803
Carbon	Pre-historic	Rhodium	1804
Sulphur	Pre-historic	Cerium	1804
Arsenic	13th Cen.	Iridium	1804
Bismuth	15th Cen.	Osmium	1804
Zinc	16th Cen.	Potassium . . (isolated)	1807
Antimony . . .	15th Cen.	Sodium . . . (isolated)	1807
Phosphorus	1674	Calcium . . . (isolated)	1808
Cobalt	1735	Strontium . . (isolated)	1808
Platinum	1750	Barium . . . (isolated)	1808
Nickel	1754	Boron . . . (isolated)	1808
Hydrogen	1766	Fluorine [1]	1810
Nitrogen	1772	Iodine	1812
Oxygen	1774	Cadmium	1817
Chlorine . . . . . -	1774	Lithium	1817
Manganese	1774	Selenium	1817
Molybdenum	1778	Silicon	1822
Tungsten	1781	Bromine	1826
Uranium	1789	Aluminium . (isolated)	1827
Zirconium	1789	Thorium	1828
Titanium	1795	Magnesium . (isolated)	1829

[1] Fluorine was not isolated till 1886.

DISCOVERY OF THE ELEMENTS — *Continued*

Vanadium 1830	Praseodymium 1885
Lanthanum 1839	Dysprosium 1886
Erbium 1843	Gadolinium 1886
Terbium 1843	Germanium 1886
Ruthenium 1845	Argon 1894
Cæsium 1860	Helium 1895
Rubidium 1861	Krypton 1898
Thallium 1861	Neon 1898
Indium 1863	Xenon 1898
Gallium 1875	Europium 1901
Samarium 1879	Radium 1902
Scandium 1879	Lutecium 1907
Thulium 1880	Neoytterbium 1907
Neodymium 1885	

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